TECHNOLOGY

VOL 10

1973

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TECHNOLOGY

QUARTERLY BULLETIN OF THE PLANNING & DEVELOPMENT DIVISION
FERTILIZER CORPORATION OF INDIA LTD.
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Gram: PLANDEV, Sindri

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Vol. 10 JAN-MARCH & APRIL-JUNE 1973 Nos. 1 & 2

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EDITOR: S. N. ROYE
Junior Editors: BENOY K. BANERJEE & S. A. KULKARNI
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UDC 541.128.13+546.74

The susceptibility composition isotherm of nickel oxide supported on α-Al_2O_3, prepared by multiple impregnation, is presented. Magnetic susceptibility decreases due to the decrease in the dispersion. Such a decrease in the dispersion results from the saturation of the low surface area support with a monolayer of nickel oxide (NiO) particles and due to the beginning of the crystallite growth. A rise in susceptibility observed for the high nickel containing samples probably indicates the formation of nickel oxide hills. This rise has been attributed to the overcoming of the influence of the support by the deposited nickel oxide. Finely dispersed nickel oxide having no definite crystal structure did not show any antiferromagnetism, which however appeared in the catalysts with higher nickel oxide concentrations indicating the f.c.c. lattice growth. Catalytic activities for the carbon monoxide oxidation reaction supports the requirement of an 'effective dispersion'. A study on the changes in magnetization during reduction above the Curie temperature has been suggested as a method to observe the aggregation of reduced nickel particles.

Studies on Supported Nickel Catalysts— Characterization of Dispersion and Heterogeneity of the Active Component by Magnetic Measurements

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Introduction

Magnetic techniques have often been used in characterizing nickel catalysts supported on high surface carriers, both in the oxidized[1-5] and reduced[6-11] states with reference to the respective massive forms. But the most extensively studied[12-15] branches are the granulometry and effect of chemisorption on magnetization. The present investigation comprises magnetic measurements of a series of nickel oxide catalysts supported over low surface α-Al_2O_3 to characterize dispersion and surface heterogeneity. Catalytic activities have been determined for the catalysts for carbon monoxide oxidation reaction and correlated with the magnetic parameters and surface areas. The rate of change of magnetization during reduction of a poorly dispersed catalyst has also been studied and discussed.

Experimental and Results

Sample Preparation: Extruded α-Al_2O_3 rods (ignited at 1300°C. in the powdered form) were soaked overnight in 10 per cent (w/v) nickel nitrate solution, then air-dried and calcined for 6 hours at 450°C. This process was repeated until a series of 9 catalysts up to a maximum of 18.9 per cent nickel oxide were obtained. The percentages of nickel were estimated by the conventional chemical method. The massive nickel oxide was prepared by the decomposition of A.R. nickel nitrate at 450°C. for 6 hours.

Magnetic Measurements: Magnetic measurements were carried out with a Faraday-type magnetic balance. The weight-sensing device was a two-section helical quartz spring housed in an all-glass enclosure. The sensitivity of the instrument was 0.0148 mg. All the measurements were taken under running vacua (10^{-4} mm. Hg.) between 77 and 700°K. The instrument was calibrated using ferrous ammonium sulphate and sucrose. The measured susceptibilities per gram of nickel oxide at 298°K. were plotted against nickel oxide concentrations (Fig. 1A). These concentrations were calculated from the estimated nickel contents. The observed Weiss constants and the magnetic moments at 77°K. are shown in Fig. 1B. Thermomagnetic studies

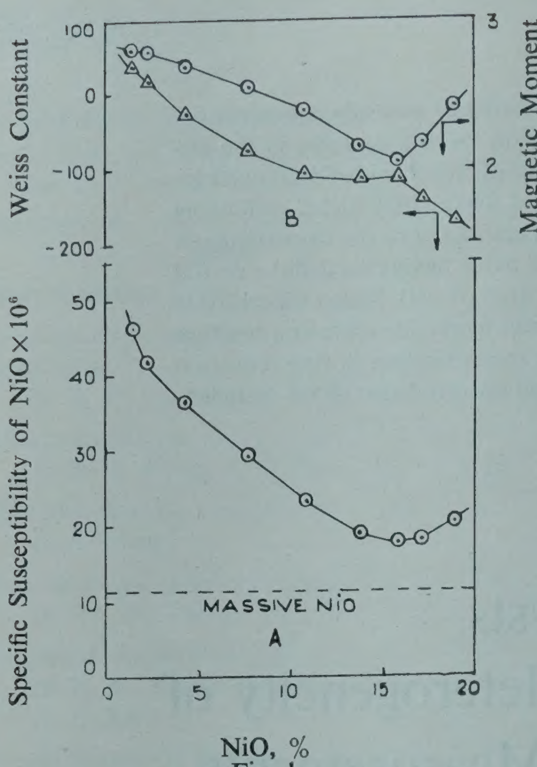

Fig. 1

A. Susceptibility-Composition Isotherm and Specific Magnetic Susceptibility of Massive Nickel Oxide

B. ⊙ Magnetic Moment at 77°K
△ Weiss constant

showed that the Néel temperatures for these catalysts approach that of the massive nickel oxide (Table 1). The broken line in Fig. 1A represents specific magnetic susceptibility of massive nickel oxide.

Reduction: Some samples were isothermally reduced at 390°C. in the spring balance in flowing hydrogen and the change in weight was noted with time. One such plot is shown in Fig. 2A-I. Further, 30 mg. of the same sample was reduced under the identical conditions and changes in magnetization observed with time are plotted in Fig. 2A-II.

TABLE 1

% NiO	Frequency of Impregnation	BET Surface Area, m²/g.	Nèel Temperature (T_N), °C.
α-Al_2O_3	0	15.6	—
1.40	1	21.0	Absent
2.15	2	17.3	Absent
4.27	3	14.5	180
7.68	4	11.2	—
10.80	5	8.3	180
13.80	6	9.8	—
15.80	7	11.6	—
17.08	8	11.8	184
18.90	9	12.1	190
100	—	—	250

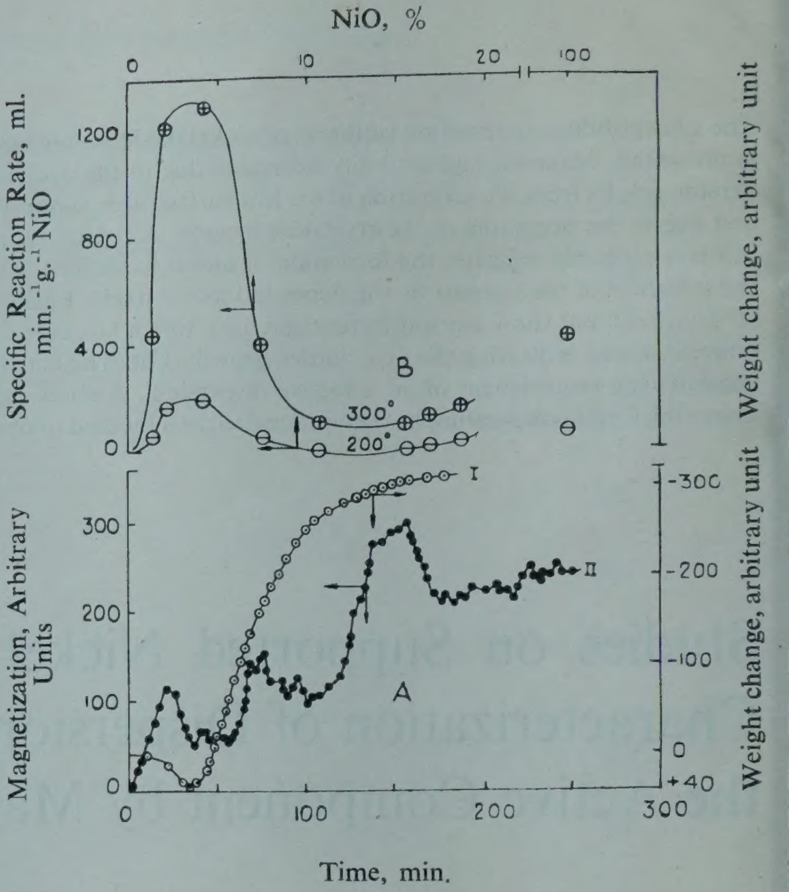

Fig. 2

A. Reduction of 6.05% NiO Catalyst
I—Without Magnetic Field, II—In Magnetic Field

B. Variation of Catalytic Activity with NiO Concentration ⊖ at 200°C and ⊕ at 300°C

Surface Area: BET areas of the support and the catalysts were determined using an automatic adsorption desorption nitrogen isotherm recorder 'Adsorptomat' (Aminco, USA). These values are given in Table 1.

Catalytic Activities: The activities were determined by studying the carbon monoxide oxidation reaction. 1.5 ml. of weighed catalyst of 60~80 mesh (BSS) size was diluted with an equal volume of powdered glass of the same size. This mixture was charged in an all-glass pulse-reactor mounted on a gas chromatograph (Griffin, UK) and heated for 30 min. in a stream of oxygen at 450°C. Oxygen was then cut off and the catalyst was purged for 30 min. with the carrier gas nitrogen, flowing at 100 ml./min. under 10 psi pressure. Pulses of 0.25 ml. gas mixture of carbon monoxide and oxygen (2:1) were injected into the carrier stream at the top of the catalyst. The kinetics of the carbon monoxide oxidation were evaluated from the first order equation[16],

$$k=\frac{F}{W}\,\text{In}\,\frac{1}{1-x} \qquad \ldots.(1),$$

where k=specific rate constant, F=rate of flow of the carrier gas in ml./min., W=weight in gram of catalyst charged in the reactor, x=degree of carbon monoxide oxidation. The values of specific rate constants were found to be consistent with different (F/W) values. The variation of specific rate constant values at 200 and 300°C. with nickel oxide content is shown in Fig. 2B.

Discussion

A transitional metal oxide, when supported on an inert material, may be distributed as finely dispersed molecules along with some molecular aggregates. The probability of such a molecular dispersion is more, if the concentration of the active component is less. However, in all the cases some amount of aggregated molecules must be present in the catalyst. In this study, nickel oxide was supported on α-Al_2O_3 by impregnating and then curing at low temperature, so that formation of the spinel ($NiAl_2O_4$) may be avoided. In this case, the nickel oxide is in a mechanical mixture with the α-Al_2O_3. Then question may arise regarding the origin of the forces which are responsible for binding the nickel oxide molecules or their aggregates to the surface of alumina. A probable answer to this fundamental question is given on the basis of observed magnetic parameters. A gradual increase of the concentration of the active component in the catalyst is shown to provide a picture of the surface structure which is developed at different stages of the nickel pickup.

The observed susceptibility values (Fig. 1A) at 298°K. show a smooth decrease with the increasing nickel concentration but in the last two samples the susceptibility values increase slightly. The other magnetic parameters, such as the magnetic moments at 77°K., the Weiss constant (Fig. 1B) and the Néel temperature (Table 1) also markedly change with the increasing nickel concentration. The susceptibility composition isotherm can be divided into three regions on the basis of magnetic parameters and BET surface areas. The first two catalysts containing low nickel oxide are superparamagnetic in nature. Because, the magnetic characteritics of massive nickel oxide, such as a Néel temperature at or below 250°C., a negative Weiss constant ($\triangle$) or a considerable amount of spin compensation are absent in these two catalysts. The absence of these antiferromagnetic characteristics implies that the deposited nickel oxide is present as finely dispersed molecules or molecular aggregates having no definite crystal structure.

The total magnetic moment (μ_{S+L}) of an isolated nickel atom or ion is 4.47 B.M. In the crystalline nickel oxide, the orbital moments are quenched to form the lattice[17] and the effective moment decreases from the spin-only value of 2.83 B.M. depending on the extent of the crystal growth. In the first two catalysts, the observed magnetic moment (2.8 B.M.) for a nickel ion accounts for the spin-only formula but there is no contribution of the orbital angular moments. This shows that the molecules of nickel oxide are bound to the surface of the support by orbital angular moments only and thus the two unpaired electrons of the surface nickel ion are stabilized by the vacant p-orbitals of the aluminium ions of the support. This seems to explain how the supported transitional metal oxides assume the crystal structure of the support which was also observed by Selwood *et al*[18, 19].

As the nickel concentration is increased, the specific magnetic susceptibility values smoothly decrease and tend to approach that of the unsupported massive nickel oxide and the observed magnetic moments at 77°K. show a decrease from 2.8 to 2.05 B.M. It also appears from the observed Weiss constants (Fig. 1B) that these values shift to the negative side showing a growth of antiferromagnetism in these samples. The growth of antiferromagnetism is further confirmed from the appearance of Néel temperatures (Table 1) in samples containing 4.27 per cent nickel oxide and above. According to Li[20], a two-dimensional nickel oxide lattice cannot sustain antiferromagnetism. A calculation based on the ionic radii of Ni^{2+} (0.78Å) and O^{2-} (1.32Å) shows that 0.0427 g. nickel oxide can cover an area of 25 m^2 when uniformly distributed as nickel oxide molecules over a flat surface. Since the surface area of the support is only 15.6 $m^2/g.$, it is obvious that a three-dimensional lattice structure has already developed in this catalyst. The BET surface areas (Table 1) support the views just mentioned. Initially for the first two superparamagnetic nickel oxide containing samples, due to fine dispersion of the active component, the surface areas of the catalysts were more than that of the support. But as soon as the alumina surface is covered with a layer of nickel oxide particles, the BET surface areas drop below that of the support, due to filling up of the pores in the support.

In this concentration region, owing to the formation of larger aggregates of nickel oxide, the interchange interaction between the unpaired d-electrons of the neighbouring nickel ions becomes predominating. These exchange interactions are affected by spin compensation responsible for antiferromagnetism in nickel oxide. Such an interaction is accompanied with the intervention of an oxide ion[21]. The orbital angular moments have no contribution in the observed magnetic moments, since these are partially quenched by the support and partially by the growing f.c.c. lattice of the nickel oxide particles.

In the remaining portion of the susceptibility composition isotherm, the magnetic susceptibility values at 298°K. show an increasing trend. The observed magnetic moments at 77°K. also increase from 2.05 to 2.4 B.M., while the Weiss constants decrease sharply. The observed change in the Weiss constants signifies the growth of nickel oxide crystallites. In a normal case, it is expected that the magnetic susceptibility and the magnetic moment both would decrease simultaneously. However, in the present case the anomaly seems to be related to an overcoming of the influence of the support by the deposited nickel oxide in this concentration region. Eischens and Selwood[18] observed that up to three atomic layers, the support influenced the chromium ions in the chromia-alumina type catalysts. On the influence of the support on transition metal ions, Selwood based his theory of valence inductivity[19] and Rymer *et al*[3] proposed a two-phase model. However, both the groups of workers[3, 19] could not observe an increase in the magnetic susceptibility at high metal concentration probably due to the use of high surface area supports.

The surface areas in the present case show an increase in the concentration region under discussion. Such an increase suggests the formation of multilayer nickel oxide hills on the surface of the support instead of a flat massive nickel oxide deposit. Further, studies on the reduction of the catalysts at 390°C. show that the reducibility increases with the increasing metal concentration. The difficulty experienced in reducing the supported nickel oxide, specially at lower concentration region, supports the influence of the carrier on the dispersed component.

The activities of the catalysts, massive nickel oxide as well as the α-Al_2O_3, which were used as the support to prepare the catalysts were examined for carbon monoxide oxidation over a temperature range 25 to 475°C. In this paper, however, the specific reaction rates (ml./min./g. nickel oxide) at two definite temperatures, viz. 200 and 300°C., are shown (Fig. 2B) to evaluate the performances of the catalysts. It should be mentioned here that the α-Al_2O_3 also responds to carbon monoxide oxidation in the temperature range 228 to 465°C. though with very low activity, showing an activation energy of 7.7 k.cal/mol. This result prompted us to check the powdered glass which was used as a diluent in the pulse reactor. The specific reaction rates for this material were negligibly small (between 0.3 and 0.6 ml./min./g.) in the temperature range 375 to 475°C. and the activation energy was found to be 7.4 k.cal/mol.

The first two catalysts containing superparamagnetic nickel oxide had no Néel temperature, so these catalysts behaved uniformly in the temperature range 25 to 250°C. But all the antiferromagnetic catalysts showed the 'Hedvall effect'[23, 24] at the observed Néel temperatures (Table 1). The results (Fig. 2B) show that the best activity is shown by the catalyst containing 4.27 per cent nickel oxide. In the first catalyst (1.4% NiO), the 50 per cent of the support surface is covered with NiO, while in the second (2.15 per cent nickel oxide), the extent of coverage is about 80 per cent assuming a molecular dispersion of nickel oxide. In the catalyst with 4.27 per cent nickel oxide, the extent of coverage is 100 per cent and also the nickel oxide around this concentration has started assuming a definite three-dimensional crystalline form. The catalytic activities are found to increase sharply with the increasing NiO distribution on the support. But as the nickel oxide lattice growth becomes predominant, the activities begin to fall as seen in the subsequent samples. The catalytic activities corresponding to 100 per cent nickel oxide (Fig. 2B) are for the unsupported massive nickel oxide. The massive nickel oxide is a polycrystalline substance, in which the electron spins are compensated amongst themselves to a large extent. But it may be observed from the activity data (Fig. 2B) that this material shows better catalytic performance than some of the supported catalysts. Therefore, it seems reasonable to assume that the influence of the support as well as the spin compensation due to the growth of antiferromagnetism govern the efficiency of a catalyst. Mooi and Selwood[24] reported a similar curve for the decomposition of hydrogen peroxide on manganese dioxide-alumina catalyst; however, a rising trend in activity at higher metal concentration was not observed by them as in the present case. This increasing trend of the catalytic performance by some of the catalysts of high metal concentrations tending to reach the activity of the unsupported polycrystalline nickel oxide may be due to an overcoming of the influence of the support.

To this end, it may be concluded that the catalytic carbon monoxide oxidation reaction requires an 'effective dispersion' of the active component over the support. The effective dispersion can be defined as an optimum amount of the metal, which should be present in the catalyst as molecules or molecular aggregates without appreciable crystalline form. This optimization can be achieved by monitoring the magnetic parameters of the supported nickel oxide catalysts during manufacture by multiple impregnation procedure.

Isothermal reduction of a poorly dispersed (6.05 per cent nickel) catalyst shows several peaks in magnetization *vs.* time of reduction plot (Fig. 2A-II). For the same sample, when isothermally reduced in absence of the magnetic field, a smooth curve (Fig. 2A-I) is obtained. This suggests that rapid rise in magnetization is due to reduction and following demagnetization is a subject of change in magnetic state, due to delocalization of unpaired d-electrons in the conduction band. This points out to be the thermal migration of the reduced nickel particles to form larger aggregates. However, such a study should be made above the paramagnetic Curie temperature, otherwise a smooth rise due to ferromagnetism will be observed[25]. This is a new technique which may be extremely useful in the study of sintering of the freshly reduced tiny nickel particles.

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[Original mss. received on Oct. 5, 1972]

UDC 541.128+542.45

Studies have been made on five industrial low temperature CO-conversion catalyst samples of the type copper oxide—zinc oxide, copper oxide-zinc oxide-alumina and copper oxide-zinc oxide-alumina-chromia. These studies include the determination of surface area, crystal phase composition, particle size of active component and the conversion efficiency. All these catalysts differ in physico-chemical parameters and the conversion efficiency was found to vary from 75 to 90 per cent. It has been observed that the copper concentration is the only parameter which has relationship with the catalyst performance.

An Assessment of Industrial Low Temperature Shift Catalysts

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In supported metal oxide catalysts, properties, such as activity, stability, etc., are likely to be dependent on concentration of the active component, its state of subdivision and phase composition, as well as the physico-chemical properties of the supporting medium. It is known that catalysts having the same physical and chemical identity may differ in performance while put to use. The evaluation of catalyst till today is greatly dependent on the actual performance tests under plant operating conditions. For an organization dealing with the development and production of catalysts and also for actual users who are required to choose the best catalyst available in the market, it is difficult to put the samples in actual operation for evaluation. Attempts are, therefore, made in different organizations to examine whether the catalytic function can be correlated to any of the parameters, which can be determined under laboratory conditions. It is known that a particular phase, which contributes to the intrinsic activity of the catalyst, may differ for different types of catalyst. It is, therefore, necessary to identify the particular phase composition of the catalyst for specific function and supported work in this connection is in progress in authors' laboratory with different types of fertilizer catalysts and the present investigation relates to the low temperature conversion catalyst. The principal object is to examine whether copper oxide is in the free state or in combination with other components of the carrier and can be identified as the active ingredient. In addition, attempts have been made to see if there is dependence of catalyst efficiency on the surface area, copper crystallite size, copper content, etc.

Experimental

Altogether five commercial varieties of low temperature CO-conversion catalyst were chosen for the present study. The catalysts have been referred hereinafter as A, B, C. D and E. Chemical analysis of these catalysts is given in Table 1.

TABLE 1—Chemical Analysis of Five Catalysts

Composition, %	A	B	C	D	E
L.O.I.	2.10	11.96	10.45	10.28	1.20
CuO	33.0	10.25	10.45	45.20	32.00
ZnO	61.0	24.60	19.00	7.00	66.00
Al_2O_3	—	52.80	19.00	24.00	—
Cr_2O_3	—	—	40.55	13.45	—

The studies on the five catalyst samples comprise: (1) crystal phase composition by x-ray diffraction, (2) particle size by x-ray diffraction, (3) specific surface area by BET method, and (4) activity test in an integral reactor.

X-ray photographs of all the catalyst samples were taken in a Guinier camera using CuKα radiation at 40 kV and 20 mA. The x-ray photographs of the samples C and D were also taken in a Debye-Scherrer camera of diam. 11.56 cm using MoKα radiation at 40 kV and 18 mA. The d-spacings were calculated and the phase identification was done by the method of Hanawalt *et al*[1].

The particle size of copper oxide and copper of different fresh and reduced samples was determined by the line broadening method using the Scherrer formula[2].

$$B = \frac{0.9\lambda}{t \cos\theta}$$

where B = broadening of diffraction line measured at half its maximum intensity (radians)
θ = Bragg angle of the diffraction line of the test sample
t = Crystallite size, Å
λ = Wave length of the x-radiation, Å

The crystal phases present in the different catalyst samples and the particle size of copper have been shown in Table 2.

TABLE 2—CRYSTAL PHASE COMPOSITIONS AND PARTICLE SIZE OF COPPER

Catalyst Sample	Crystal Phases Present		Particle Size	
	Fresh	Reduced	Fresh (CuO), Å	Reduced (Cu), Å
A	ZnO, CuO	ZnO, Cu	230	637
B	ZnO, α-Al_2O_3, H_2O, CuO.	ZnO, α-Al_2O_3, H_2O, CuO	208	259
C	$ZnCr_2O_4$, $CuCr_2O_4$, α-Al_2O_3.	$ZnCr_2O_4$, Cu, $Cu_2Cr_2O_4$, α-Al_2O_3	—	55
D	CuO, $CuCr_2O_4$, α-Al_2O_3. H_2O. ZnO*	Cu, Cu_2O, ZnO, α-Al_2O_3. H_2O, Cr_2O_3 (Trace).	170	249
E	ZnO, CuO	ZnO, Cu.	208	273

*The state of aggregation of zinc could not be definitely established. Fine subdivision of ZnO or $ZnCr_2O_4$ may be present in the bulk composition of the fresh catalyst.

Activity Test: The activity tests were carried out in an all-glass apparatus similar to the one described earlier[3]. The catalyst pellets were crushed and sieved to obtain granules of -10 to $+14$ mesh (B.S.S.) size. The tests were conducted under the following fixed conditions: (i) gas composition (%) v/v—CO_2 17-18, CO 7-8, H_2 56-58 and N_2+CH_4 rest; (ii) steam-to-gas ratio 1.0; (iii) reactor temperature 220°C, (iv) S.V. (dry gas) 2,000 and (v) pressure 1.0 atm. The results have been shown in Table 3, which also gives surface area data.

Results and Discussion

Dependence of Activity on the Crystal Phase Composition: It can be seen from the results that the catalyst samples differ widely as regards chemical composition (Table 1), crystal phase composition (Table 2), surface area and conversion efficiency (Table 3).

TABLE 3—CONVERSION EFFICIENCY AND SURFACE AREA

Catalyst Samples	% CO Converted	Surface Area, m^2/g.	
		Fresh	Reduced
A	88	20.8	19.0
B	75	160.0	96.0
C	80	56.4	50.0
D	90	78.0	75.0
E	88	36.8	30.0

There are two samples (A and E) which comprise two-component systems and are identical in chemical composition, crystal phase composition and activity.

The only three-component system studied is the sample B, in which the α-Al_2O_3, H_2O phase is present in addition to zinc oxide and copper oxide phases.

The remaining two samples (C and D) are four-component systems and as such are more complex in nature. Although these two samples contain the same chemical ingredients in varying amounts, their phase composition is different. Copper (II) chromite is the only common phase found to be present in these cases.

The crystal phase composition of the sample C comprises zinc chromite, copper chromite and alpha aluminium oxide whereas the crystalline phases present in the sample D are copper oxide, copper chromite and alpha aluminium oxide hydrate. Zinc oxide of fine subdivision or zinc chromite may be present in the bulk composition of the fresh catalyst samples C and D respectively. The presence of these phases could not definitely be established due to the general broadness of the x-ray diffraction pattern of the samples.

The crystal phase composition of all the reduced samples shows the presence of elemental copper indicating that either copper oxide (CuO), copper chromite ($CuCr_2O_4$) or both have been reduced. In the samples A, B, E and D, copper oxide present in the fresh sample is reduced directly to copper. The reduction mechanism in the cases of C and D is different from that of A, B and E. In these cases, besides copper oxide, copper chromite is also reduced. The argument in favour of the reduction of copper chromite is evident from the disappearance of copper chromite phase and appearance of chromium oxide (Cr_2O_3) phase in the reduced sample of D. The chromium oxide phase in the reduced sample of C could not be identified probably due to the following reasons: (i) the chromium oxide content released is less, or (ii) it is present in an amorphous state. Further, the presence of cuprous chromite phase in the reduced sample of C indicates that partial reduction of $CuCr_2O_4$ has taken place in this sample.

It is evident from the above results that the three samples A, E (two-component system) and B (three-component system) contain the same active phase, viz. copper, and the appearance of copper in the reduced state is attained by the same mechanism. But the catalytic efficiency of samples A and E is more than that of B. It may be noted here that the samples having higher copper content are more active than the other containing less copper, which indicates that the concentration of copper may play a part in the activity of the catalyst irrespective of two-or three-component systems.

The two four-component samples, viz. C and D, contain other catalytically active components, viz. copper chromite ($CuCr_2O_4$) and zinc chromite ($ZnCr_2O_4$) besides copper oxide. Saleta *et al*[4] have observed that in the system zinc oxide-copper oxide-chromia, the activity of the catalyst depends on the amount of zinc chromite (in the form of spinel). The activity increases with increasing amount of zinc chromite. Yur'eva *et al*[5], using the same system, have also noticed that the higher activity is due to the formation of copper and zinc chromite.

On the basis of the observations made by the above workers[4,5], the samples C and D are supposed to be more catalytically active than the other samples by virtue of their having chromite phase. But the conversion efficiency of the sample C was found to be less than A and E and the sample D have comparable activity with that of A and E. This clearly shows that presence of either copper or zinc chromite besides copper oxide and zinc oxide does not increase the activity for water gas shift reaction. Thus, on the basis of the observed data the present authors could not confirm the observation of the earlier workers. Again, it is interesting to note here that of the two samples C and D, the latter is more active than C, although both contain the same ingredients and the chromite phase. The main difference between them is that sample D has higher copper content than C, indicating again that the conversion efficiency has certain relationship with the copper content, as has been stated earlier.

The conclusion which emerges from the x-ray investigation is that crystal-phase composition alone cannot provide the clue about the quality of the catalyst and the knowledge of the copper content appeared to be more important for assessing the low temperature CO-conversion catalyst.

Dependence of Activity on Copper Content: Comparing the conversion efficiency of all the samples, it appears that the samples in which copper concentration is around 10 per cent (samples B and C) have conversion efficiency less (75-80 per cent) than others (88-90 per cent) having copper concentration above 30 per cent, irrespective of crystal phase composition and the presence of other catalytically active components besides copper oxide. Further, a combination of higher copper content (beyond 30 per cent) and presence of chromite phase also does not substantially increase the catalytic efficiency as can be seen in the case of sample D.

Dependence of Activity on Surface Area: The surface area of the fresh and reduced samples varies from 20.8 to 160 m^2/g. and 19 to 96 m^2/g. respectively. It can be seen from comparison between the surface area and conversion efficiency that the sample having highest surface area (sample B) is less active than the one having the lowest surface area (sample A). Further, the samples A, D and E differing widely in their surface area exhibit about the same conversion efficiency.

The catalytic efficiency is expected to increase with increase in the surface area but for low temperature conversion catalyst it is not safe to rely on surface area data for selection of a good catalyst.

Dependence of Activity on the Particle Size of Copper: It can be seen from Table 2 that copper is invariably present in the reduced samples and its particle size varies widely.

Tsuchimoto *et al*[6] have shown that the activity of the copper catalysts depends on the particle size of copper. But the results indicate that the sample A having highest particle size of copper is more active than C having lowest particle size of the copper. Further, it is also noticed that although the conversion efficiency of D and E differs from that of B, they have their particle size of copper in almost the same range. This anomalous behaviour in the conversion efficiency-particle size relationship may be either due to the widely different nature of the samples, or the size ranges observed may be within the optimum limit where the conversion efficiency is not affected by the particle size.

Conclusion

It has been observed that physico-chemical parameters like phase composition, surface area and particle size of active component are not adequate for correct assessment of low temperature CO-conversion catalyst. Of all the parameters studied, chemical identity, particularly the copper content, appears to have some bearing on the performance of the catalyst. It has also been observed that optimum copper oxide content lies somewhere between 30 and 45 per cent. Further, the result of the present investigation can be utilized as guidelines for selection of a good catalyst. A catalyst user is most of the time inclined to select those which are having highly developed surface, fine subdivision of active component and in addition information relating to presence of such phase which is sometimes identified as active component. The information provided in the present investigation can keep a user sufficiently informed about the danger of depending on any one of the parameters mentioned.

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[Original mss. received on Oct. 12, 1972]

UDC 541.128+546.72+546.75

Promoter action of alumina on the conventional ferric oxide-chromium oxide catalyst for water gas shift reaction has been studied. It was observed that the presence of alumina tends to lower the activity and there is a gradual decline in activity with increase in the percentage of alumina in the system. However, alumina, even in small concentration, enhances the thermal stability of the catalyst, particularly at higher reaction temperatures.

Effect of Alumina on the Structural and Thermal Stability of Conventional Iron-Chromia Catalyst

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Deactivation of the catalyst is a major concern in the development and operation of an industrial catalytic reactor. Sustained activity is one of the vital factors for the success of a commercial catalyst. In high temperature water gas shift reaction catalyst, chromium oxide is most commonly used as a structural promoter with ferric oxide to impart stability to the catalyst and in effectively arresting the grain growth of ferric oxide, when reduced to Fe_3O_4[2,4,7]. In spite of the presence of chromium oxide, the stability of the catalyst declines at a faster rate in prolonged run in plants, particularly when the shutdown and recommissioning of the converters are frequent.

Alumina is another structural stabilizer which can be used in catalyst preparation, the advantages being its high melting point, refractory nature[4], high specific surface area and its ability in preventing the catalyst from deactivation by heat[6]. It has been further reported that alumina facilitates reduction of ferric oxide to hydrated oxide but prevents further reduction to metallic iron[6].

The effect of addition of alumina on structural properties and stability of ferric oxide-chromium oxide catalyst has not been well studied so far. The present investigation is concerned with the role of alumina on the stability and activity of the conventional shift reaction catalyst. Attempts have been made to draw a correlation between energy of activation and activity in terms of conversion efficiency, with particular reference to increasing alumina concentration in the mass. The function of alumina in stabilizing the gross structural properties of ferric oxide-chromium oxide system and in arresting the decline in activity under higher operating temperatures has been discussed. Samples prepared by incorporating 2-8 per cent alumina in the ferric oxide-chromium oxide system were tested for activity both at higher and lower temperatures. Decline in activity with prolonged run at higher temperature has been studied to assess the comparative thermal stability. It was observed that the presence of alumina tends to lower the activity of the catalyst. There is a gradual decline in activity with increase in the percentage of alumina in the mass. The activation energies were found to vary from 24.43 to 26.5 k.cal/mol. for the different samples. Pre-exponential factor A was found to diminish with increase in the percentage of alumina. It was further observed that presence of alumina contributes towards thermal stability, particularly at higher reaction temperatures.

Experimental

Catalyst Preparation: Six samples were prepared by incorporating varying amounts of alumina into the ferric oxide-chromium oxide system. The incorporation was affected by intimate mechanical mixing of precipitated ferric oxide with chromic acid and aluminium nitrate solution.

The ferric oxide was obtained from ferrous sulphate solution by precipitating with ammonium bicarbonate. After complete precipitation the slurry was filtered, washed with hot water until free from sulphate. The cake, thus obtained, was dried and further heated at 400±10°C. for a few hours to convert the hydrated oxide to ferric oxide which contained 2-3 per cent free moisture. The three components, iron oxide, chromium oxide and aluminium nitrate, were intimately mixed to make a paste which was then dried in an air-oven at 119±5°C., granulated and pelleted to 6×6 mm. size. The pellets were finally heat treated at 425±10°C. to convert the salts into their oxides.

Chemical Analysis: Samples were analysed for chemical composition by standard methods[1] (Table 1).

Samples from D_1 to D_4 contain both chromium oxide and aluminium oxide, D_5 contains ferric oxide and chromium oxide and is free from alumina whereas D_6 contains ferric oxide and alumina but no chromia.

Measurement of Physical Parameters: The mechanical strength of the pellets, surface area, pore volume and pore size distribution were measured as given below: (a) **Mechanical strength**—Crushing strength (Table 1) was measured by a tensometer. (b) **Surface area**—Surface area was determined with the help of nitrogen adsorption isotherm at liquid nitrogen temperature by applying the B.E.T. equation. (c) **Pore volume and pore size distribution**—Total pore volume of the samples was determined from the difference of mercury and helium displacement values. Pore size distribution was determined by mercury penetration method using an Aminco-Winslow porosimeter having a working pressure range up to 15,000 lbs/sq. in.

Activity Measurements: (a) **Description of the apparatus**—A schematic diagram of the apparatus used for testing the activity is shown in Fig. 1. The synthesis gas is drawn from a gas holder and after it passes through a surge vessel (S), is allowed to enter the saturator. By means of a perforated tube the gas is allowed to bubble through the water in the saturator which ensures complete saturation. Steam-to-gas ratio is maintained by controlling the saturator temperature at a predetermined level. The gas, thus saturated with steam, is allowed to enter the reactor R through a gas inlet valve (V). The reactor (R) consists of a stainless steel block of 50 mm. O.D. and 600 mm. length inserted in a vertical tubular furnace E (50 mm. I.D.×500 mm. long). Both inlet and outlet pipelines are drawn from the bottom of the reactor, which is designed to keep the catalyst bed temperature in an isothermal condition. The bed is fixed above the outlet line by means of a wire gauge, inserted at a suitable position inside the reactor. The gas enters the bed from the top of the reactor. The advantage with this reactor is that the gas is adequately preheated before coming in contact with the catalyst bed and the bed temperature is maintained isothermal. The catalyst bed temperature is controlled by an energy regulator. The two thermocouples (T_1 and T_2) indicate both bottom and top layer temperatures respectively of the catalyst bed. The gas with the required amount of steam is allowed to enter the bottom

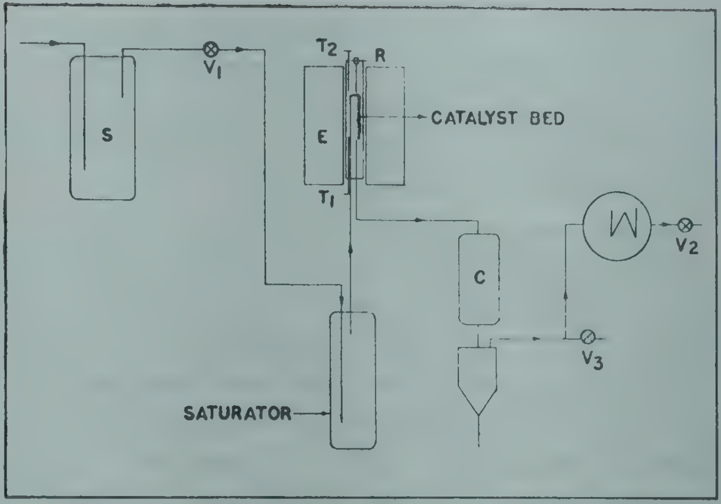

Fig. 1—Schematic Diagram of the Activity Testing Unit

TABLE 1—CHEMICAL COMPOSITION

Catalyst Sample	Fe_2O_3, %	Al_2O_3, %	Cr_2O_3, %	Loss at 900°C, %	Bulk Density, g./cc.	Crushing Strength, kg./cm².
D_1	88.2	1.98	6.96	2.84	1.1993	160
D_2	86.14	4.02	6.94	2.92	1.1543	169
D_3	84.16	5.97	6.89	3.12	1.136	185
D_4	81.74	8.06	7.02	3.15	1.1021	187
D_5	90.1	0.0	7.06	2.90	1.4325	79
D_6	89.74	7.04	0.0	3.24	1.0572	110

of the reactor and after passing through the catalyst bed at a fixed temperature, it enters condenser (C) and is then metered by a gas meter (W) before finally being vented through a valve (V_2). The gas samples are taken from valve V_3 and analysed.

The activities of all the six catalyst samples were tested at atmospheric pressure and temperatures varying from 300 to 425°C. at an interval of 20°C. up to 380°C. and finally at 425°C. The temperature of the catalyst bed was maintained in an isothermal condition as indicated by the two thermocouples provided at the top and bottom. Sized catalyst (−20, +25 mesh) was charged in each experiment. This size was selected to avoid internal diffusion restrictions. A space velocity of 20,000 hr^{-1} (vol. of dry gas at NTP/unit vol. of catalyst/hr) was used to allow the reaction to take place in the kinetic zone. The steam-to-gas ratio was maintained at about one. The average inlet gas composition (in percentage) is as follows: CO_2: 8-9, CO: 30-32, H_2: 37-39 and N_2: 20-22. The activities are expressed in terms of specific rate constant calculated by applying the following expression given by Uchida[2]. Assuming that the reaction follows first order kinetics,

$$k = V(R+1) \ln\left(1 - \frac{n_x}{n_{eq}}\right)$$

where V = Space velocity
R = Steam-to-gas ratio
n_{eq} = Theoretical percentage of conversion
n_X = Percentage conversion observed experimentally
k = Specific rate constant.

The activation energies are calculated by plotting log k against 1/T (Fig. 2).

Assessment of Thermal Stability: To assess the effect of alumina on thermal stability two samples D_1 and D_5 were heat treated at 600°C. for 8 hours and then their physical parameters were measured. This temperature was chosen in consideration of the fact that deactivation of the conventional catalyst proceeds at a faster rate above 575°C. The effect of increase in the alumina content of the catalyst on its thermal stability was also studied by giving a prolonged run of 250 hours at a higher reaction temperature of 500°C. Activity was measured at an interval of 24 hours to estimate the rate of decline in activity with time.

Results and Discussion

(a) The bulk density, being an additive property, will depend on the composition, particle density and compactness of the components in the mass. It may be seen from the results (Table 1) that addition of alumina to higher density iron oxide (sp. gr. of alumina 3.59 and that of iron oxide 5.12) lowers the bulk density of the catalyst. There has been a continuous fall in bulk density with increasing concentration of alumina in the catalyst mass and this value has come down by 20-22 per cent in case of the sample containing 8 per cent alumina.

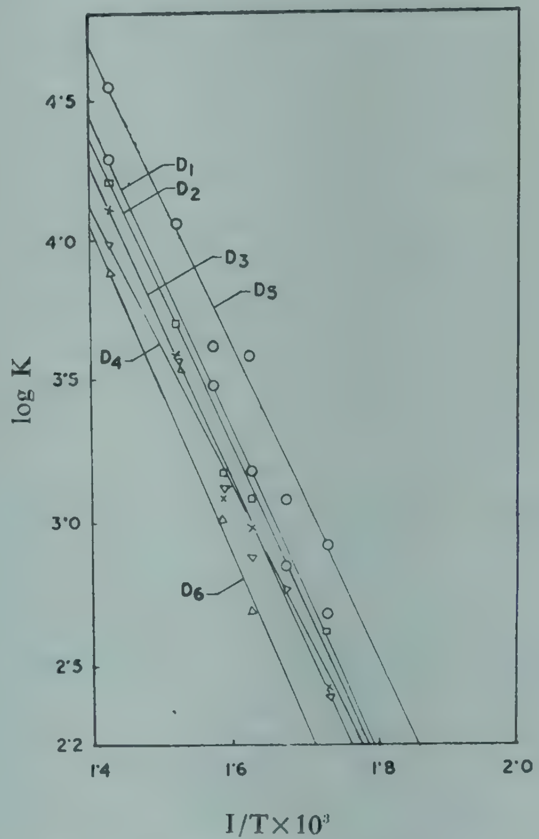

Fig. 2—Arrhenius Plots of Activation Energy

There has been a remarkable improvement in the mechanical strength of the tablets by the addition of alumina in the ferric oxide-chromium oxide system (Table 1); the crushing strength has increased more than two-fold by only 2 per cent alumina. Further increase in alumina concentration from 2 to 8 per cent has, however, only marginal effect on the strength. The results (Table 1) further show that for obtaining higher mechanical strength presence of both alumina and chromia in the mass is desirable. But alumina appears to have greater contribution to the ultimate strength of the pellet than chromia.

(b) *Activity*: Activity as percentage conversion and specific rate constant calculated on the basis of the expression suggested by Uchida are given in Table 2. The activation energy (E) and pre-exponential factor (A) obtained by plotting log k against 1/T (Fig. 2) have

TABLE 2—COMPARATIVE ACTIVITY AT DIFFERENT TEMPERATURES

Sample No.	300°C		320°C		340°C		360°C		380°C		425°C		Value of E, k/cal/ mole	Value of A/hr × 10³
	% Conv.	K/hr × 10³	% Conv.	K/hr × 10³	% Conv.	K/hr × 10³	% Conv.	K/hr × 10³	% Conv.	K/hr × 10³	% Conv.	K/hr × 10³		
D_1	1.42	0.462	2.3	0.680	4.54	1.887	9.7	3.014	25.0	9.022	54.1	19.291	24.93	28.84
D_2	1.40	0.395	2.24	0.709	3.66	1.179	4.25	1.479	14.0	5.099	43.2	15.874	25.57	24.49
D_3	0.70	0.253	0.24	0.699	2.94	0.937	3.52	1.215	10.9	3.870	35.8	12.856	25.98	19.28
D_4	0.65	0.236	1.34	0.572	1.93	0.729	3.3	1.279	9.7	3.688	23.3	9.560	26.31	13.61
D_5	2.63	0.826	3.61	1.175	5.86	2.279	10.48	4.160	27.4	11.360	67.2	35.008	24.45	51.29
D_6	No Activity				0.45	0.481	0.926	1.005	3.14	3.492	6.47	7.750	28.94	11.78

also been included in the same table. It may be seen that energy of activation is only slightly affected by the incorporation of alumina in the catalyst mass. There is a positive upward trend in the E values with increasing concentration of alumina (Fig. 3) and the value has risen from 24.5 k.cal/mol. (without alumina) to 26.1 k.cal/mol. (with 8 per cent alumina). It is interesting to note that although the energy of activation remains practically constant, the conversion efficiency is affected considerably by the addition of alumina in the system. This apparent anomaly can be accounted for, if the pre-exponential factor A for different catalysts (Fig. 4) is taken into consideration. The values of A obtained from the intercepts of Arrhenius plot were found to diminish sharply with addition of alumina, but the rate of decrease of these values is not proportional to the increasing concentration of alumina in the samples. This is clearly shown in Fig. 4, which depicts the change in the value of pre-exponential factor (A) with increasing alumina content of the catalyst. Introduction of about 2 per cent alumina in the system has brought a sharp drop in the value of A but with further increase of alumina concentration, the downward slope of the curve loses its steep character.

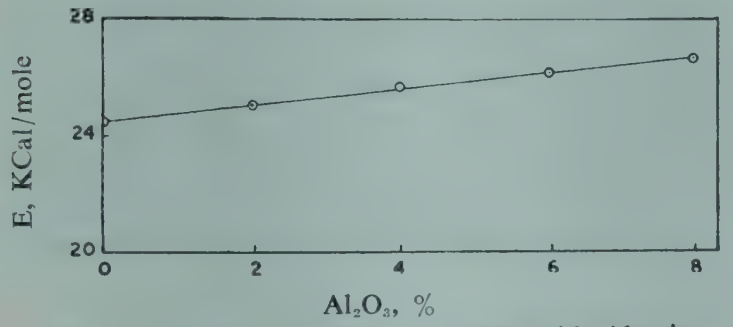

Fig. 3—Change in Activation Energy with Alumina Content of the Catalyst

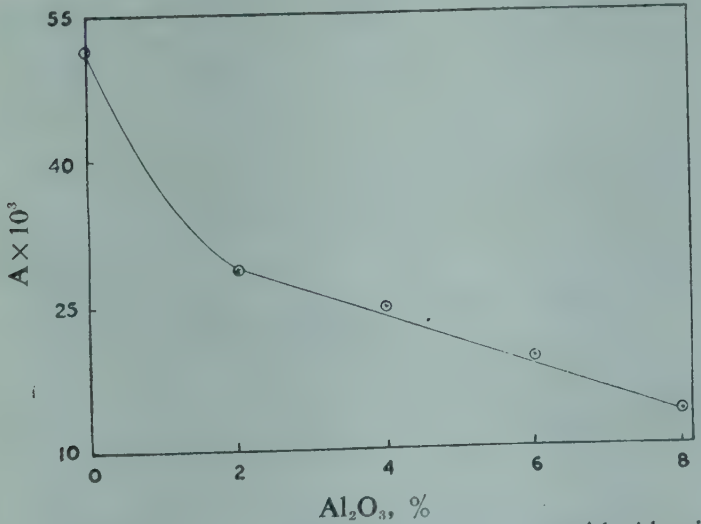

Fig. 4—Variation of Pre-exponential Factor with Alumina Content of the Catalyst

The Arrhenius behaviour significantly throws light on the change in the state of the catalyst surface caused by the introduction of alumina in the system. The temperature response of the various samples as evidenced by the slope of Arrhenius plot shows that the nature of the active centres has not been modified qualitatively which, if it occurs, is likely to be reflected in the pattern of the temperature rate constant curves (Fig. 2). This will imply that a change in E values will accompany modification of the active centres. It is significant that although the E values show moderate or no change, pre-exponential factor has decreased on introduction of alumina in the system. At higher concentration of alumina the decline in A values appears to bear a greater proportionality with alumina content. The fairly constant value of the activation energy shows that the nature of the active sites remains unchanged by the addition of alumina. On the other hand, the lowering of the Arrhenius frequency factor suggests that the surface concentration of the active sites decreases with the introduction of alumina in the system and this appears to be the main reason for the lower conversion efficiency of alumina-bearing catalysts.

Table 2 shows the comparative activity of the catalyst samples, specific rate constant (k), energy of activation (E) and pre-exponential factor (A). It is interesting to observe that the catalyst sample prepared without chromia is virtually inactive at lower temperatures but at higher temperatures some activity is noticeable. Introduction of alumina in the iron-chromia system produces a deteriorating effect on the conversion efficiency and specific rate constant, which is particularly pronounced at lower temperatures. The gap between the activities of the ferric oxide-chromium oxide and ferric oxide-chromium oxide-alumina types of catalysts narrows down at higher reaction temperatures. It may be observed that the intrinsic activity of iron-chromia catalyst is always higher than the three-component catalyst containing alumina under the conditions studied. It appears that incorporation of alumina to the extent of 2 per cent may be advisable for increased thermal stability and mechanical strength with marginal sacrifice of the initial activity.

(c) *Thermal Stability*: To assess the effect of alumina on the thermal stability, samples D_1 and D_5 were heat treated at 600°C. for 8 hours. The results of surface area and pore size distribution (Table 3) clearly indicate that the presence of alumina prevents shrinkage in surface area to a great extent. While surface area in the case of D_5 came down from 67.5 m^2/g. to 14.9 m^2/g., the same for D_1 came down from 71.0 to 41.4 m^2/g. only. The percentage shrinkages in the two cases are about 78 and 43 respectively. The shrinkage in smaller pores up to 200 Å exhibits a similar trend, the percentage shrinkages being about 88 and 20 respectively without and with alumina. The results further point to a notable change in the pore size distribution, especially with the finer pores. With sintering at higher temperature, the smaller pores were practically destroyed in case of the sample without alumina (D_5), giving rise to pores of the size 500 Å and above. This can be contrasted with the effect of high temperature sintering of D_1 having only 2 per cent alumina; the growth of bigger pores at the expense of smaller ones is comparatively much less and limited to 100 Å only.

The comparative thermal stabilities of alumina-bearing catalysts were studied in yet another way. The samples D_1 and D_5 were given a prolonged run at higher reaction temperature (500°C) under reduced condition. After activation in reducing atmosphere the surface areas of both alumina-promoted catalyst (D_1) and the one without alumina (D_5) were found to attain almost identical values, viz. 13.6 m^2/g. (Table 4). But the two types of catalysts differ from each other in more than one way. Firstly, the porosity of the reduced ferric oxide-chronium oxide catalyst drops by about 17-19 per cent. In contrast, the same for the alumina-promoted catalyst remains almost unchanged after reduction. Secondly, the change in the pore spectrum is different for alumina-bearing catalysts. Shrinkage of finer pores up to 300 Å is 41.6 per cent in case of ferric oxide-chromium oxide catalyst, whereas it is comparatively less, only 28 per cent, for the sample containing only 2 per cent alumina. The effectiveness of alumina

TABLE 3—Effect of Recuring at 600°C for 8 Hours

Sample Description	Surface Area, m^2/g.	Total Pore Volume, cc./g.	Pore Size Distribution, %						
			4-60Å	60-100Å	100-200Å	200-300Å	300-400Å	400-500Å	500-75000Å
D_1 Fresh	71.0	0.2580	26.0	21.2	27.3	13.7	4.5	1.7	5.4
D_1 Recured	41.4	0.2790	13.6	14.3	32.0	21.9	9.0	3.9	5.9
D_5 Fresh	67.5	0.3542	14.1	14.6	18.5	11.1	9.8	7.7	23.8
D_5 Recured	14.9	0.1834	3.4	0.4	2.0	8.9	11.5	14.4	58.2

TABLE 4—Change in Surface Area and Porosity on Prolonged Use

Sample Description	Surface Area, m^2/g.	Total Pore Volume, cc./g.	Pore Size Distribution, %							Shrinkage in Pores up to 200 Å, %	Shrinkage in Pores up to 300 Å, %
			4-60Å	60-100Å	100-200Å	200-300Å	300-400Å	400-500Å	500-75000Å		
D_5 Fresh	65.6	0.3542	14.1	14.6	18.5	11.1	9.8	7.7	25.8	—	41.6
D_5 Used	13.6	0.2941	1.3	1.5	12.6	18.6	15.9	14.5	35.4	67.4	—
D_1 Fresh	71.0	0.2580	26.0	21.2	27.3	13.7	4.5	1.7	5.4	—	28.0
D_1 Used	13.7	0.2527	6.8	1.9	23.7	31.6	19.2	6.5	10.0	56.5	—

in stabilizing the activity becomes clear when the conversion efficiency of the two samples in prolonged runs is compared (Table 5). It may be seen that in 250 hours' continuous run the activity of D_5 dropped by 18 per cent but under the same operating conditions activity of D_1 dropped by only 5.5 per cent. From the above study, it can be concluded that alumina lowers the intrinsic activity of iron-chromia catalyst but improves its thermal stability.

TABLE 5—CHANGES IN ACTIVITY WITH TIME AT 500°C

Time, hrs.	D_1		D_5	
	% Conversion	$K/hr \times 10^3$	% Conversion	$K/hr \times 10^3$
25	77.3	74.75	79.9	63.10
49	75.1	57.34	77.2	61.25
73	75.6	60.20	76.7	60.80
96	75.5	60.24	72.7	41.27
120	73.7	58.58	70.5	35.26
170	72.8	48.54	66.0	34.16
220	73.0	47.81	65.5	34.54

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[Original mss. received on Oct. 26, 1972]

UDC 541.128+546.74+546.621: 542.46

The physico-chemical properties of a co-precipitated alumina-based nickel oxide catalyst cured at different temperatures for a fixed period have been investigated. With increasing calcination temperature the mechanical strength has been found to improve whereas the surface area falls steadily. The activity of the catalysts for hydrogen peroxide decomposition decreases and the excess oxygen, estimated iodometrically, falls with increasing temperature. A linear relationship has been observed between a logarithmic plot of excess oxygen and surface area.

Influence of Heat Treatment on a Nickel-on-Alumina Catalyst: Changes in Physical Properties and Activity

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Heat treatment is an important step in the manufacture of a catalyst. In this step, several changes, like decomposition, dehydration and phase changes, etc., may occur. Besides, changes in physical parameters, like specific surface area, pore volume, pore size distribution, density and mechanical strength, also take place. The electron donating or accepting capacity of catalysts of semiconductor family is also affected in this step.

Physico-chemical properties of thermally-treated unsupported nickel oxide have been investigated by a number of workers[1-3]. However, it will not be logical to extrapolate the results of heat treatment on the bulk compound to that of the supported catalyst[4] in view of the fine dispersion of the active component on the surface of the latter.

The changes accompanied by thermal treatment are also dependent on the method of preparation of the catalyst. Nath *et al*[5] have made a comparison between the ground and calcined samples with respect to physical properties and their reducibility in hydrogen. Arora *et al*[6] have shown an empirical relationship between the surface area and excess oxygen for samples prepared by mechanical mixing and by impregnation. The present work was undertaken to study the physico-chemical changes that a co-precipitated alumina-nickel oxide catalyst undergoes during progressive heat treatment. The nickel oxide, being a p-type semiconductor, has the excess oxygen associated with it and in this, nickel exists in two oxidation states (Ni^{2+}/Ni^{3+}) forming a reduction potential of the system. The system is thus suitable for oxidation-reduction reactions. In the present work the decomposition of hydrogen peroxide has been used as a measure of activity.

Experimental

Preparation: The catalyst was prepared by co-precipitation from a solution of nickel nitrate and aluminium nitrate. After the process of washing, kneading and granulation etc., cylindrical tablets of 10×10 mm. size were made. These tablets were cured at different temperatures for eight hours.

Surface Area and Pore Size Measurements: The specific surface areas were determined by low temperature adsorption of nitrogen by the BET method. The pore size distribution was measured in a mercury porosimeter having a working pressure range up to 5,000 psi. The average particle size and pore radius were calculated as described earlier[7].

Crushing Strength: The crushing strength was measured by a Hounsfield tensometer. The pressure was applied on the two flat faces of the cylindrical tablet until it was crushed. The average value of ten tablets was taken as the standard crushing strength.

The volume of a single tablet was measured by the water displacement method.

Excess Oxygen Determination: Iodometric method[14] of Bunsen & Rupp was employed for the estimation of excess oxygen. A weighed amount (1-2 g.) of the sample was placed in 100 ml. of distilled water, and 20 ml. of hydrochloric acid (conc.) was added. 2 g. of potassium iodide was then added and the mixture allowed to stand for 15 min. in a neutral atmosphere of nitrogen. The brown suspension was then titrated with standard sodium thiosulphate $\left(\frac{N}{100}\right)$

Activity Determination: The activity was determined in an apparatus similar to one suggested by Nachmann[8]. The reaction was carried at the room temperature (25°C). The suspension of catalyst in 5 ml. of hydrogen peroxide (6 per cent) was stirred by a magnetic stirrer. Catalyst weight was so adjusted as to keep the evolution of oxygen around 0.2 ml. in 15 min. Under these conditions a constant concentration of hydrogen peroxide may be assumed. The amount of oxygen liberated was measured with time. The integrated form of the zero order rate equation $V_t = V_o + kt$ was used, where V_o and V_t are the volume of oxygen liberated initially and after time 't' respectively. The rate constants have been computed from the slope, when V_t is plotted against 't'.

Results and Discussion

The surface area, pore size distribution, average particle size and pore radius are tabulated in Table 1. It is seen that with increase in calcination temperature the surface area gradually falls, whereas the average particle size and pore radius increase. The total pore volume remains almost unchanged, but the percentage distribution of the pores follow a regular pattern. The percentage of bigger pores greater than 500 Å radius gradually increases with temperature of calcination. Higher temperature causes the smaller pores to collapse resulting in bigger pores. With increasing temperature this effect is more. The process results in the diminution of specific surface area. Consequently, the average particle size and pore radius increase.

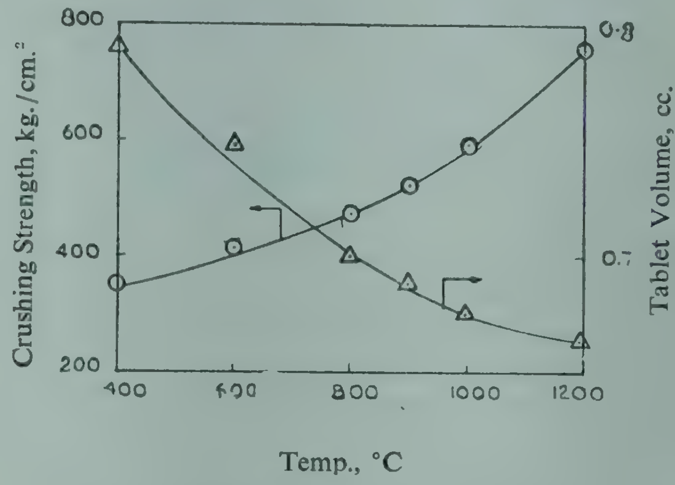

Fig. 1 Variation of Crushing Strength and Tablet Volume with Curing Temperature

In Fig. 1, the variation in volume of a tablet and the dependence of mechanical strength on calcination temperature are illustrated. The treatment of the catalyst at a higher temperature for eight hours results in setting in and mutual adjustment of imbalanced stresses, imparting more stability to the product. This results in the volume shrinkage of a tablet with rise in temperature. The phenomena can be compared to the familiar process of annealing. At higher temperatures, as indicated earlier, the small particles coalesce to form bigger particles. This process is accompanied by an overall reduction in dimensions. From the industrial point of view, in addition to activity, a knowledge of these two properties is essential as they markedly influence the

TABLE 1—SURFACE AREA, PORE VOLUME, AND PORE SIZE DISTRIBUTION

Sample cured at °C	Total Porosity, cc/100cc.	S. Area, m²/g.	Average pore radius, $\bar{r}_p$ Å	Average grain, radius $\bar{r}_g$Å	Pore size distribution, % by vol.				
					4—175 Å	175-300 Å	300-400 Å	400-500 Å	500-75000 Å
400	44.7	68.3	63.2	117.0	69.5	10.2	4.1	3.1	13.1
600	44.6	55.3	77.8	145.0	71.8	9.1	3.8	2.4	12.9
800	49.2	44.9	110.2	170.0	63.9	12.5	4.6	2.8	16.2
900	49.4	34.8	143.5	220.0	62.6	11.6	4.3	2.7	18.8
1,000	47.6	28.0	166.0	274.0	49.6	18.3	6.1	3.6	22.4
1,200	44.4	12.1	320.0	600.0	10.6	22.4	18.9	16.0	32.1

life of the catalyst and design of converters. The relationship between surface area and crushing strength is shown in Fig. 2. The strength varies linearly with surface area.

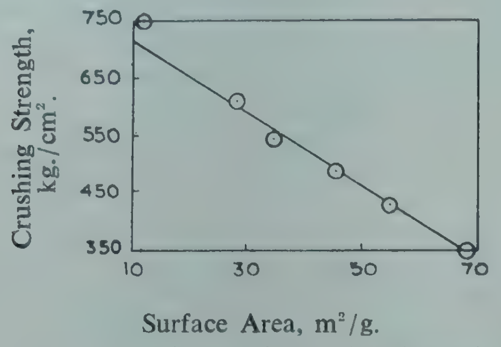

Fig. 2—Variation of Crushing Strength with Surface Area

The variation of excess oxygen (in % atom) and activity for hydrogen peroxide decomposition with change in calcination temperature are shown in Fig. 3. Both excess oxygen and activity fall with increase in the temperature of calcination. Different authors have studied the phenomenon of excess oxygen in nickel oxide[9-12]. During the decomposition of nickel salts in air, excess oxygen appears in the lattice as well as chemisorbed on the surface. Few authors[13,14] have sought the possibility of derivation of specific surface area of metals and metal oxides from a measurement of excess oxygen content. According to Peers[13], in case of nickel oxide, for majority of samples cured at temperatures higher than 500°C, the value of active oxygen content is practically equal to the surface excess oxygen. He suggested the following empirical equation.

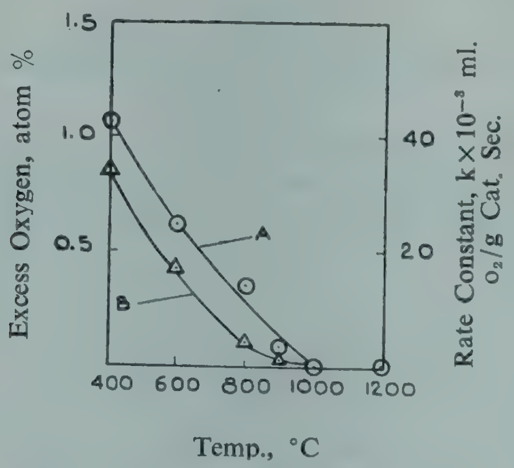

Fig. 3—Plot of Excess Oxygen (A) and Rate Constant (B) with Temperature

$$\log S = \log P + 1.55$$

where S = specific surface area

and P = active oxygen content.

In the present case, assuming the excess oxygen (O) to be equal to the active oxygen content, it is to be seen that a plot of log S against log O gives a straight line. This plot is shown in Fig. 4. The fall in the excess oxygen content is rapid, similar to that in nickel oxide.

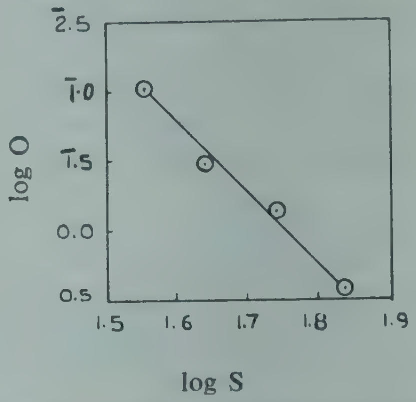

Fig. 4—Variation of Excess Oxygen with Surface Area

The excess oxygen that is present in nickel oxide formed by thermal treatment is accompanied by the creation of Ni^{3+}, which is black in colour. The mechanism is as follows:

$$2O^{2-} + 2Ni^{2+} + \tfrac{1}{2}O_2(g) \rightleftharpoons 2Ni^{3+} + 3O^{2-} + C$$

where C is a cationic vacancy.

The concentration of Ni^{3+} is responsible for the rate of decomposition of hydrogen peroxide. In the present study the activity is represented in terms of the rate constant k. The concentration and quantity of hydrogen peroxide and the amount of catalyst is so chosen that there is no appreciable change in the concentration of peroxide during decomposition. Hence a zero order rate equation has been assumed for the calculation of rate constants. In the light of the equation cited above, it appears that at higher temperatures the backward reaction is facilitated resulting in a diminution of the excess oxygen and Ni^{3+} ions. This results in a fall in the excess oxygen and activity at higher temperatures.

The decomposition of hydrogen peroxide is based on the existence of two oxidation states of nickel, forming a reduction potential of the system. The peroxide is decomposed by its oxidation through the step[15]

$$H_2O_2 = HO_2 + H^+ + e.$$

The free radical sets off the chain reaction[16]

$$HO_2 + H_2O_2 = OH + H_2O + O_2$$

$$OH + H_2O_2 = HO_2 + H_2O.$$

The chain is terminated by the reaction

$$OH + HO_2 = H_2O + O_2.$$

The available electron from the oxidation of hydrogen peroxide is received by Ni^{3+}.

The mechanism of the decomposition of H_2O_2 has been discussed by many workers[17,18]. Treatment of the nickel oxide at higher temperatures converts more and more Ni^{3+} species into Ni^{2+}. Therefore, lower activity is obtained for the sample when calcined at a high temperature. The degree of activity represented by the value of rate constant k is associated with the amount of excess oxygen. Both fall almost linearly with temperature in most of the temperature range.

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[Original mss. received on May 30, 1972]

UDC 542.924–16: 541.128.34

A modified and more rigorous derivation of Ozawa's equation regarding thermal decomposition of solids has been proposed. The theoretical thermograms have been used to show the application of the proposed relation in obtaining kinetic data, which have been shown to be more accurate.

On the Evaluation of the Apparent Activation Energy of Solid State Decomposition Reactions

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Inroduction

The thermogravimetric data provide valuable information regarding heat treatment processes of solids, which is very useful in the design and control of industrial heat treatment operations of catalytic solids, because it speaks unambiguously about the various stages of physico-chemical changes, like the dehydration, decomposition, etc. The thermogravimetric data are also employed in the evaluation of the energy of activation and the frequency factor of solid state decompositions. However, none of the methods available in literature[1-4] are simple and free from assumptions of a decomposition model envisaging a hypothetical reaction mechanism. It may be pointed out that no significant meaning can be assigned to the order of reaction and the frequency factor in solid state decomposition reactions. On the other hand, the activation energy of the reaction is a direct measure of the energy changes involved.

This study is an attempt to present a theoretical basis for the evaluation of activation energy from simple experimental data without taking resort to any decomposition model. The method proposed is a versatile one and an improvement over the existing techniques.

The decomposition reaction is generally represented by the equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \qquad \ldots \quad (1)$$

where α = the fraction decomposed,

t = time,

k = specific rate constant,

and n = the order of the reaction.

Now from Arrhenius equation,

$$k = A \exp\left(-\frac{E}{RT}\right) \qquad \ldots \quad (2)$$

Substituting for k in (1)

$$\frac{d\alpha}{dt} = \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \qquad \ldots \quad (3)$$

In some of the methods[1,2], the relation (3) is treated as a differential equation and the fractional decompositions are obtained by integration of the equation. In another group of methods[3,4], the kinetic constants are obtained from the plots of the logarithms of the terms of equation 3.

It may be noted that both the above types of methods are cumbersome and elaborate mathematical operations must be performed to evaluate the kinetic parameters. Moreover, not all the solid state decomposition reactions can be characterized by equation (1). This is because of the fact that in addition to the mass changes described by this equation, a number of energy rearrangements[5] may also take place during the reaction, such as due to nucleation, and adsorption of the gaseous species surrounding the solid. The decomposition rates may also be influenced by the diffusion[6,7] of the surrounding gaseous molecules into and the products of decomposition out of the crystal lattices of the solid. In view of these complications, the effects of particle size, gaseous atmosphere around the sample, moisture content and other factors make the right hand term of equation (1) a complicated function of α. This necessitates a modification of this term according to the possible mode and mechanism of the decomposition, and calculation of the kinetic data is made by trial and error method of fitting the curves or by graphical evaluation of the relevant factors. Satava[8] has discussed a method based on these considerations where the correct function of α is determined by obtaining the best fit curve by plotting six or seven various functions of α against T previously derived by considering various models of decomposition, incorporating nucleation and diffusion factors.

Theoretical

Ozawa[9] developed an approximate integral method which does away with the complex function of α and relates the kinetic parameters to the heating rates employed in obtaining the thermograms. In this method, the fractional weight W is represented as a function of the fraction of a structural quantity like a functional group, a constituent or a broken bond, etc. Thus,

$$W = f(\alpha) \qquad \ldots \quad (4)$$

The term $(1-\alpha)^n$ in equation (3) can be represented by $g(\alpha)$ an unknown function.

$$\text{Therefore,} \ \frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) g(\alpha) \qquad (5)$$

By integrating and making an approximation for the smaller reaction rates at low temperatures, Ozawa[9] suggested that:

$$\int_{T_o}^{T} \exp\left(-\frac{E}{RT}\right) dT = \int_{O}^{T} \exp\left(-\frac{E}{RT}\right) dT \qquad \ldots (6)$$

By representing the integral at the right hand side as a function p and assuming that the value of $\frac{E}{RT} > 20$, Doyle[10] showed that

$$\log p\left(\frac{E}{RT}\right) \approx -2.315 - 0.4567\,\frac{E}{RT} \qquad \ldots (7)$$

On the basis of these considerations, Ozawa found that

$$-\log a_1 - 0.4567\,\frac{E}{RT_1} \doteq -\log a_2 - 0.4567\,\frac{E}{RT_2} \qquad \ldots (8),$$

where a_1 and a_2 are the heating rates and T_1 and T_2 are temperatures for the corresponding heating rates for a given value of fraction decomposed.

A comparison of a family of equations of type (8) for different heating rates yields the value of E.

In the present paper it is shown that a more general form of equation (8) can be derived without taking resort to any approximation and also without assuming any decomposition model.

Derivation of the Equation

In a reaction of the type $aA_s \rightarrow bB_s + cC_g$, ..(9)
the rate of disappearance of A is expressed by equation (1). As has been reviewed earlier, in actual practice the kinetic equation is more complex because the mechanism of the reaction is influenced by a number of factors other than the law of mass action, viz, adsorption, nucleation and diffusion. It is, therefore, reasonable to replace the term on the right hand side of equation (1) by a function f (α), which includes all the factors influencing the decomposition rate.

The proposed equation is derived as follows:

Equation (1) can be rewritten as

$$\frac{d\alpha}{dt} = k\ f(\alpha) \qquad ..(10)$$

or, $$\frac{d\alpha}{dT}\frac{dT}{dt} = k\ f(\alpha)$$

or, $$\frac{d\alpha}{dT} = A\ \exp.\left(-\frac{E}{RT}\right) f(\alpha) \qquad ..(11)$$

where k has been replaced by the exponential and preexponential terms from the Arrhenius equation and 'a' is the rate of heating. For two different heating rates, a_1 and a_2, two such equations can be written as

$$\left(\frac{d\alpha}{dT}\right) a_1 = A\ \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad ..(12)$$

and $$\left(\frac{d\alpha}{dT}\right) a_2 = A\ \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad ..(13)$$

Now, for a given value of α, the values of temperatures for the heating rates a_1 and a_2 become T_1 and T_2. The equations (12) and (13) can, therefore, be rewritten as

$$\left(\frac{d\alpha}{dT}\right)_1 a_1 = A\ \exp\left(-\frac{E}{RT_1}\right) f(\alpha) \qquad ..(14)$$

and $$\left(\frac{d\alpha}{dT}\right)_2 a_2 = A\ \exp\left(-\frac{E}{RT_2}\right) f(\alpha) \qquad ..(15)$$

Combining the above two relations we get,

$$\exp\left[\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right] = \left(\frac{d\alpha}{dT}\right)_2 a_2 \Big/ \left(\frac{d\alpha}{dT}\right)_1 \times a_1 \qquad ..(16)$$

Taking logarithms of both sides we get,

$$\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = 2.303 \log \frac{(d\alpha/dT)_2}{(d\alpha/dT)_1}\ \frac{a_2}{a_1}$$

or, $$E = 2.303\ R.\log\left[\frac{(d\alpha/dT)_2\ a_2}{(d\alpha/dT)_1 .\ a_1}\right] \Big/ \left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad ..(17)$$

The equation (17), therefore, can be conveniently employed in the evaluation of the apparent activation energy E by comparing the thermograms obtained at two different heating rates.

It is found that for different heating rates, the thermograms run more or less parallel to each other. Therefore, for the parallel portions of the thermograms the ratio of the tangents on the right hand side of equation (17) becomes unity i.e.,

$$\frac{(d\alpha/dT)_2}{(d\alpha/dT)_1} = 1$$

For these portions of the thermograms E can be evaluated from the eqn. (18) given below in which the heating rates and the temperature corresponding to a given value of α are the experimental quantities which can be easily determined.

The equation (17), therefore, reduces to one derived by Ozawa.

$$E = \frac{2.303\ R}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \log\left(\frac{a_2}{a_1}\right) \qquad ..(18)$$

This clarifies the nature of the approximation used in the derivation made by Ozawa. Moreover, while Ozawa assumes that $\frac{E}{RT}$ should be more than 20 for his approximation to be valid, no such condition is needed in the present mode of derivation. It is obvious that the above equation does away with the measurement of the rate of change of α with temperature which otherwise would be a tedious graphical procedure. This equation can be utilized satisfactorily to obtain a reasonably accurate value of the activation energy of a given reaction It may, however, be pointed out that the relation, $\left(\frac{d\alpha}{dT}\right)_2 \Big/ \left(\frac{d\alpha}{dT}\right)_1 = 1$ is again an approximation, the validity of which is worth checking. The above ratio is actually less than unity, as the curves with higher heating rates tend to lean towards the temperature axis. This invariably results in higher values of E than expected.

Application

The analysis of the equation (17) made it necessary to draw a set of idealized thermograms. They were derived by assuming that the value of E is 25 K cal/mole for a given reaction and the frequency factor A is 10^9. Now, for heating rates 1,2 and 10°C/min., it is possible to construct theoretical thermograms assuming the following kinetic equation:

$$1 - (1 - \alpha)^{1/2} = kt \qquad \ldots\ldots \qquad (19)$$

The curves are shown in Fig. 1. The equation (18) was applied for the analysis of these curves. The values of E obtained for the various values of α ranging from 0.1 to 0.9 are listed in Table 1. The values calculated using equation (19) are 5 to 15 per cent higher than the theoretical value of 25 K cal/mole. This discrepancy points out the fact that the ratio $\left(\frac{d\alpha}{dT}\right)_2 \Big/ \left(\frac{d\alpha}{dT}\right)_1$ in equation (17) cannot, in fact, be taken exactly equal to unity. It is significant to note that at values of $\alpha < 0.1$, the value of E is very high when the equation (18) is applied. It seems, therefore, necessary that the above ratio must be determined experimentally and incorporated in equation (18). Since it is not possible to measure this ratio accurately over the entire range of α, as an approximation it is proposed that the ratio of the values of the slopes of secants drawn by joining the two extreme values of α (the range for which the value of E is to be determined), can be taken as a good measure of the average ratio of the decomposition rates. However, caution may be exercised in selecting the range of α values, because of the uncertainty regarding the initial portion of the thermogram and also of the large differences between the slopes of the tangents in this portion of the curves being compared. For this reason, it may not be advisable to consider points below $\alpha = 0.1$ for the calculation of E. When the ratios of the decomposition rates are to be incorporated, equation (17) may be taken as the final form for the evaluation of the value of E. The average of the ratios of the decomposition rates for the curves 1:2 and 1:3 (Fig. 1), were found to be 0.94 and 0.83 respectively. Table 1 shows the values of E corrected by incorporating this ratio. It may be seen at once that the average value of E, over $\alpha = 0.1$ to 0.9 is 25.6 K cal/mole as against the average value of 28.2 K cal/mole obtained from the approximate equation (18) for $\frac{a_2}{a_1} = 2$.

Similarly, for $\frac{a_3}{a_1} = 10$, the corrected average value of E using equation (17) is 25.3 K cal/mole while the uncorrected value is 27.5 K cal/mole. Thus, leaving the correction factor in the present case has yielded values of E higher by 5-15 per cent than the correct value.

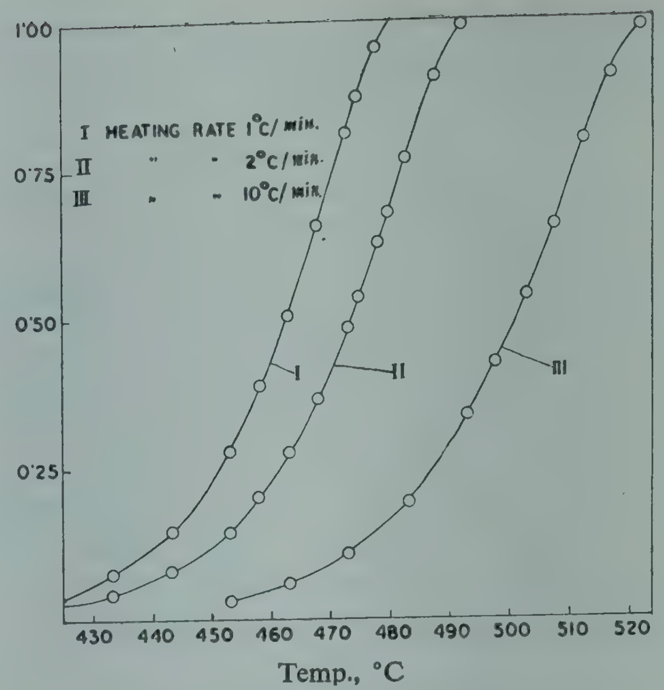

Fig. 1—Theoretical TG Curves

Conclusion

In absence of a correct knowledge of the nature of solid state thermal decomposition reactions, it has been shown theoretically that a fairly accurate estimate of the activation energy of the reaction can be made by using a simple relationship which uses a comparison between thermograms obtained at two or more different heating rates. The only experimental quantities required are the heating rates, temperatures at any given value of α and the average ratio of the rates of decomposition over a wide range of α. This average ratio is determined by making a simple approximation. The method for the calculation of E proposed here is an improvement over that of Ozawa, in that it is more versatile and accurate, yielding values very close to the theoretical ones.

TABLE 1—COMPARATIVE KINETIC PARAMETERS

α	a_2/a_1		a_3/a_1	
	E_{oz}	E_{corr}	E_{oz}	E_{corr}
0.1	28.9	26.3	27.5	25.3
0.2	28.3	25.7	25.9	25.6
0.3	29.9	26.3	27.7	25.5
0.4	28.3	25.2	27.5	25.3
0.5	27.7	26.7	27.7	25.5
0.6	28.9	25.7	27.4	25.2
0.7	28.3	25.2	27.5	25.3
0.8	27.7	24.2	27.5	25.3
0.9	—	—	26.9	24.7
Average	28.2	25.6	27.5	25.3

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[Original mss. received on Oct. 19, 1972]

UDC 541.128: 545.2: 546.74: 546.41

A rapid titrimetric method using EDTA has been developed for the estimation of nickel and calcium when present in a mixture of nickel, calcium and aluminium, and extended for the estimation of nickel and calcium in reformation and hydrogenation catalysts. The method makes use of masking agents, such as tartaric acid for aluminium. ammonium biflouride for calcium and aluminium, potassium cyanide for nickel, employing murexide and Eriochrome-Black T (EBT) as indicators.

Complexometric Determination of Nickel and Calcium in Gas Reformation and Hydrogenation Catalysts

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The conventional methods for the estimation of nickel and calcium in a mixture of nickel, calcium and aluminium are time-consuming and elaborate. Routine analyses and quality control involved in the development and production of catalysts containing these elements require very frequent estimations of the said components. It is, therefore, considered necessary to adopt a quicker and more accurate method for the estimation of nickel and calcium, when present together along with aluminium.

The direct EDTA titration procedures for the determination of nickel or calcium are well-known[1,2]. Pribil reported that triethanolamine[3] or ammonium bifluoride[4] could be used as a screening agent for aluminium. Petrovsky[5] has reported that by using cyanide and combination of other masking agents, nickel can be determined indirectly in presence of magnesium, zinc and manganese. Bukhtiarov[6] has described the EDTA titration method for the determination of calcium in nickel base alloy, using diethyl dithiocarbamate as a masking agent for nickel. Langford[7] has used sodium cyanide to mask nickel for determination of calcium and magnesium in nickel plating solution. The method of estimation of nickel in supported nickel catalysts,[8] Raney nickel catalyst[9] and copper-nickel catalyst[10] have also been described in the literature. In these methods nickel has been estimated either by back-titration of excess of EDTA or by titrating the acid solution of nickel dimethylglyoximate precipitate with EDTA solution. In nickel-aluminium-zirconium alloy[11], nickel has been estimated directly after masking aluminium and zirconium by sodium fluoride solution using murexide as indicator.

No systematic procedure has so far been reported for the estimation of nickel and calcium in a mixture of nickel, calcium and aluminium by EDTA titration. In the present study the suitability of EDTA titration procedures has been investigated for the estimation of these components in a mixture by selective masking of the elements. Nickel was titrated directly with EDTA, masking calcium and aluminium with ammonium bifluoride and using murexide as indicator. Similarly, total calcium and nickel was titrated masking aluminium with tartaric acid. Calcium was directly estimated with EDTA at pH 10 using EBT as indicator after masking aluminium with tartaric acid and nickel with potassium cyanide. These methods have been successfully applied to the estimation of nickel and calcium in the alumina-based reformation and hydrogenation catalysts.

The results (Table 1) show that the maximum percentage deviations for nickel and calcium are within the limits of analytical error. So, it is evident that the recommended EDTA titration method can be satisfactorily employed for the estimation of nickel and calcium in a mixture of nickel, calcium and aluminium over a wide range of proportions of all the three elements.

The procedure provides a method of titration of either nickel or calcium or sum of both by selective masking of aluminium, calcium and nickel. It is noteworthy that estimation of nickel by direct titration and calcium by difference is more simple and better suited for the purpose of frequent analysis, as it avoids the use of the dangerous chemical, potassium cyanide.

The estimations of nickel and calcium in reformation and hydrogenation catalysts, following the recommended procedures, are found to produce results (Table 2) comparable with those obtained by the conventional methods, deviations being always within 1 per cent. The time taken for analysis is about 1 hour by EDTA titrations compared to 6 to 8 hours by the conventional methods, which is a considerable advantage particularly when frequent analyses are involved.

Experimental

Reagents: The following reagents, all of A. R. quality, were used: 10 per cent potassium cyanide solution, tartaric acid (solid), ammonium bifluoride (solid), 2M sodium hydroxide solution, nitric acid (conc.), hydrochloric acid (conc.), hydrochloric acid (1:1), ammonia

TABLE 1—DETERMINATION OF NICKEL AND CALCIUM IN PRESENCE OF ALUMINIUM (SYNTHETIC SOLUTIONS)

0.05M Solution Taken, ml.			0.05M Solution Found for, ml.					Deviation, % ml.				
Al	Ni	Ca	A Ni+Ca	B Ni (direct)	C Ca (direct)	A-C Ni (by difference)	A-B Ca (by difference)	A	B	C	A-C	A-B
5.0	1.29	13.15	14.38	1.20	13.22	1.23	13.18	−.06	−.09	+.07	−.06	+.03
3.5	5.88	10.46	16.45	5.80	10.54	5.91	10.57	+.11	−.08	+.08	+.03	+.11
10.7	7.56	5.21	12.70	7.55	5.30	7.40	5.15	−.07	−.01	+.09	−.16	−.06
20.7	10.67	3.49	14.12	10.60	3.42	10.70	3.52	−.04	−.07	−.07	+.03	+.03
1.8	16.88	1.37	18.32	16.95	1.45	16.87	1.37	+.07	+.07	+.08	−.01	0

TABLE 2—DETERMINATION OF NICKEL & CALCIUM IN REFORMATION AND HYDROGENATION CATALYSTS

Sl. No.	Particulars of Sample	Nickel, %			Calcium, %			Deviation, %			
		B (Direct)	A-C (by diff.)	Conventional Method	C (Direct)	A-B (by diff.)	Conventional Method	B	A-C	C	A-B
1.	Reformation Catalyst	6.010	6.021	5.980	0.746	0.743	0.742	+0.501	+0.68	+0.53	+0.13
2.	-do-	8.415	8.419	8.398	3.351	3.357	3.346	+0.20	+0.25	+0.14	+0.33
3.	-do-	11.720	11.720	11.715	3.795	3.810	3.790	+0.04	+0.04	+0.13	+0.52
4.	Hydrogenation Catalyst	17.017	17.107	17.101	0.658	0.656	0.658	−0.49	+0.04	0	−0.30
5.	-do-	14.490	14.502	14.430	0.883	0.880	0.885	+0.42	+0.49	−0.22	−0.56
6.	-do-	12.620	12.625	12.620	1.634	1.641	1.632	0	+0.038	+0.12	+0.55

solution (1:10), 0.5 per cent methyl red solution, murexide-sucrose solid mixture (1:50), 0.2 per cent Eriochrome Black T (EBT) solution and ammonium hydroxide—ammonium chloride buffer (pH 10).

Standard Solutions: 0.05M EDTA, 0.05M calcium nitrate, 0.05M nickel nitrate and 0.05M magnesium nitrate solutions were prepared from analytical grade chemicals and properly standardized.[1] 0.05M aluminium nitrate solution—An weighed quantity of pure aluminium metal foil (E. Merck, proanalysi) was dissolved in nitric acid, boiled to expel the nitrous fumes and diluted to the calculated volume.

Analyses were carried out on synthetic solutions of aluminium, nickel and calcium and two types of catalysts. The catalysts being alumina-based, a portion of the alumina went into solution along with nickel and calcium during acid treatment for the preparation of solution. The catalyst samples used were of commercial variety.

Preparation of Catalyst Sample Solutions: About 1.5g. of finely ground catalyst sample in each case was treated with *aqua regia*, evaporated to dryness and again digested with 15 ml. of hydrochloric acid (1:1), separated from insoluble alumina by filtration and the volume was made up to 250 ml.

Determination of Nickel and Calcium: To a test solution diluted to 50 ml., two drops of methyl red indicator and 2M sodium hydroxide solution were added until the solution became yellow. About 1 g. of tartaric acid was then added whereby the solution turned red, followed by addition of 0.05g. of murexide-sucrose mixture and dil. ammonia solution until the solution was again yellow. The resulting solution was titrated with 0.05M EDTA. Near the end-point (when the solution turned red) more dil. ammonia solution (10 ml.) was added and again titrated with EDTA finally to a violet coloration at the end-point. The volume of titrant (A) was noted and was used for the estimation of either nickel or calcium by difference.

Direct Determination of Nickel: The procedure as described in the previous paragraph was followed except that about 1g. solid ammonium bifluoride was added instead of solid tartaric acid. Nickel was directly estimated from the volume of EDTA consumed (B).

Direct Determination of Calcium: To the sample solution, 10 ml. of 0.05M magnesium nitrate solution was added, followed by 0.5 g. solid tartaric acid, 20 ml. of ammonia-ammonium chloride buffer (pH 10), 20 ml. of 10 per cent potassium cyanide solution and 5 to 6 drops of EBT indicator (0.2 per cent solution) and was titrated with 0.05M EDTA solution to a colour change from wine red to pure blue. The amount of calcium was calculated directly from the titre (C) obtained by deducting the volume of EDTA consumed for magnesium solution added.

Apart from estimation of nickel and calcium by direct titration with EDTA, amounts of nickel and calcium were also calculated from the titre values A-C and A-B respectively. A number of synthetic solutions containing widely varying proportions of nickel, calcium and aluminium have been analysed following the above procedures and the results have been shown in Table 1.

Similarly, the solutions of catalyst samples have also been analysed following the same procedures as well as by the conventional methods (nickel gravimetrically as nickel dimethylglyoximate and calcium volumetrically after precipitating as calcium oxalate). These results are shown in Table 2.

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[Original mss. received on Sept. 27, 1972]

UDC 541.128: 542.46: 541.127.2

External mass transfer resistance over a commercial copper oxide-zinc oxide type low temperature shift conversion catalyst has been studied with regard to gas velocity, reaction temperature, catalyst particle size and reactor diameter. Mass transfer factors have been evaluated following three different approaches: (i) fundamental approach based on partial pressure difference between reactants in bulk phase and at interface; (ii) from an empirical relationship derived by Ruthven from a knowledge of apparent rate constant, linear velocity of gas and catalyst particle diameter; and (iii) Wheeler's equation based on the assumption that all gases have the same viscosity and same Schmidt number. No significant resistance to mass transfer has been found over the range of experimental conditions studied.

Evaluation of External Mass Transfer Resistance in Laboratory Reactor

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The criterion of designing adiabatic commercial catalytic reactor is associated with problems like correct evaluation of local mass and energy transfer parameters and determining the relation between the intrinsic and overall activities of the catalyst. It has now been well established that catalytic processes are functions of the intrinsic activity of the catalyst and the transport process to and from the catalyst surface because of the fact that depending upon the flow conditions of the reactant to the active surface of the catalyst, mass transfer can greatly affect the rate of conversion over an otherwise highly active catalyst. This will lead to erroneous conclusion about the activity of the catalyst.

Both the catalyst manufacturer and user are equally concerned that the catalyst is thoroughly evaluated with regard to its optimum performance in commercial converters. Small scale laboratory integral reactors are commonly used to determine catalytic activity under simulated commercial conditions in respect of space velocity, temperature, pressure, feed composition, etc. Experience shows that the data obtained may match those of industrial converters depending upon whether mass and energy transfer factors are of the same order as prevailing in industrial reactors. Therefore, before translating these data to predict the behaviour of industrial reactors, an examination of the extent of their applicability is necessary.

The major difference that is likely to arise between the performances of laboratory integral and industrial reactors is that mass velocities differ widely though the space velocity may remain the same. Low mass velocity may give rise to interphase mass transfer resistance; this, however, is almost entirely eliminated under commercial conditions where mass velocity of the feed is very high (for example, in the modern shift reactors, it is of the order of about 1400-1800 $g.hr^{-1}cm.^{-2}$). When the catalyst happens to be highly active, the interphase mass transfer resistance in laboratory reactors is likely to be more pronounced. For a highly active catalyst having considerable volume of finer pores the reactant will react before it can diffuse very deep into a pore of the catalyst, so that partial pressure of the reactant will fall to zero at a short distance from the external surface within the catalyst; as a consequence, drop in partial pressure of the reactant will tend to develop within the pellet. A partial pressure gradient is also developed between the main gas stream and the external catalyst surface. In such a situation, the reaction rate is controlled entirely by the rate at which reactants can be brought upto the surface and products removed. The optimum efficiency of a highly active catalyst is, therefore, exhibited when the exterdiffusion restriction is minimum.

Ruthven[1], in an analysis of the magnitude and effect of external mass transfer on overall rate of water gas shift reaction on conventional chromia-promoted iron oxide catalyst, showed that the magnitude of external mass transfer resistance was negligible under the conditions of most industrial reactors. Since the activity of the low temperature copper oxide-zinc oxide type shift conversion catalyst working in the temperature zone of 180-250°C is several-fold more than that of iron oxide-chromia catalyst, one may expect that interphase mass transfer effect might be significant.

With this end in view, the present paper aims at assessing the external mass transfer factor over a commercial copper oxide-zinc oxide type low temperature shift conversion catalyst in a laboratory reactor with regard to reaction temperature, gas velocity, catalyst particle size and reactor diameter. The established procedures[1-3] have been used for the purpose.

Experimental

A commercial low temperature copper oxide-zinc oxide catalyst was taken for the present investigation. Five different sets of experiments with varying ratios of bed length to reactor diameter with 6×6 mm. catalyst particles were undertaken to estimate the catalytic activity. Two reactors of 2.55 and 5.6 cm I.D. were employed; three bed lengths, 6.0, 10.0 and 19.0 cm. from the former and two bed lengths, 5.0 and 10.0 cm from the latter reactor made up the five sets of bed lengths. To study the effect of particle size, experiments were conducted with 3×6 mm. catalyst size.

All the experiments were conducted under atmospheric pressure with a steam-to-gas ratio of 0.5. Reaction temperatures were kept in the range 160 to 220°C. Feed gas, of the following average composition (% by volume dry gas) was obtained from the steam reformation of naphtha: carbon dioxide 15-17, carbon monoxide 13-15, hydrogen 66-68 and methane 3-5. Isothermal reaction conditions with a variation of ±2°C in temperature at the top and bottom of the bed were maintained. Other pertinent details of the experiments were identical with those in our earlier publication[4].

Results

The rate constant, taking the rate to be of first order with respect to carbon monoxide, was calculated from Moe[5] equation. The magnitude of the external mass transfer resistance was evaluated by the following methods.

(*a*) *Partial Pressure Drop method*: The partial pressure drop of limiting reactant carbon monoxide was calculated from a relation as developed below.

In the flow system at steady state, the rate of external mass transfer is equal to the rate of reaction, provided both the rates are expressed in terms of the same component, i.e.

$$r = K_G\, a\, \phi\, (P_g - P_i) \qquad \ldots(1)$$

where, r = reaction rate, g.moles hr^{-1} $vol.^{-1}$,
K_G = mass transfer co-efficient, g.moles $cm.^{-2}$ hr^{-1} $atm.^{-1}$
a = external surface area of the bed, $cm.^2/cm^3$,
ϕ = shape factor of catalyst particle, 0.91 for cylindrical tablets,
P_g = partial pressure of the reactant in the fluid, atm.,
P_i = partial pressure of the reactant at the interface, atm.

The reaction rate may be replaced by the amount of per cent conversion of the reactant, carbon monoxide for the present case.

$$\text{Thus, reaction rate} = G_M \times \text{degree of conversion.}$$
$$= G_M \times \text{mole fraction of } CO \times \frac{\%\ \text{Conv.}}{100} \qquad \ldots(2)$$

where G_M = molal mass velocity, g.moles hr^{-1} cm^{-2}.
From (1) and (2) we get

$$(P_g - P_i) = \frac{G_M \times \%CO \times \%\ \text{Conv.}}{150 \times 100 \times K_G \times a \times \phi} \qquad \ldots(3)$$

The total number of moles in the reaction mixture was 150.

The mass transfer co-efficient K_G can be calculated from the data on mass transfer relation. Studies of mass transfer from gases to pellets in fixed beds have been reported by various investigators as graphs of J_D vs. Reynolds number and as given by Satterfield[6], for a wide range of Reynolds number, $N_{Re}\ 3 < N_{Re} < 2{,}000$.

$$J_D = \frac{0.357}{\epsilon N_{Re}\ 0.359}$$

$$\text{again,} \quad J_D = \frac{K_G\, P\, N_{Sc}^{2/3}}{G_M}$$

$$= \frac{K_G\, N_{Sc}^{2/3}}{G_M}, \text{ (for 1 atm. pressure)}$$

where, ϵ = voidage in the bed = 0.4 for uniformly sized particles.

$$N_{Re} = \frac{dG}{\mu} = \text{Reynolds number.}$$

$$N_{Sc} = \frac{\mu}{\rho D} = \text{Schmidt number.}$$

At the working conditions, for naphtha-reformed gas viscosity(μ)=1.68×10^{-4} g.cm.$^{-1}$sec^{-1}, (ρ) density=0.67×10^{-3} g.cm.$^{-3}$ (ntp) and D, diffusivity = 0.35 cm.^{2}sec^{-1}. Schmidt number of the naphtha-reformed gas, from the above values comes out as 0.7. Taking N_{Sc} to be unity, we get from the above two relations

$$K_G = \frac{G_M \times 0.357}{\epsilon \times N_{Re}^{0.359}} \qquad \ldots(4)$$

The external surface area, a, of the bed is given by

$$a = \frac{6 \times L \times (1-\epsilon)}{d} \qquad \ldots(5)$$

where, L = bed height, cm.
d = particle diam. = 0.7348 cm. for 6×6 mm. tablets.

Putting the relevant figures, and inserting equations (4) and (5) in equation (3) and simplifying,

$$(P_g - P_i) = \frac{1.676\times10^{-5}\times\%CO\times\%\,Conv.\times N_{Re}^{0.359}}{L}\ \text{atm.} \qquad \ldots(6)$$

P_g, the partial pressure of carbon monoxide in the gas phase, where S/G is 0.5, is given by

$$P_g = \text{mole fraction} \times \text{pressure}$$
$$= \frac{\%\,CO}{150} \times \text{pressure}$$

When the pressure is atmospheric,

$$P_g = 0.66\times10^{-2}\times\ \%\,CO\ \text{atm.} \qquad \ldots(7)$$

From (6) and (7),

$$\frac{(P_g - P_i)}{P_g} = \frac{2.517\times10^{-3}\times\ \%\,Conv.\times N_{Re}^{0.359}}{L} \qquad \ldots(8)$$

Equation (8) gives the ratio of the drop in partial pressure at the interface to the partial pressure of the limiting reactant carbon monoxide in the gas phase. For a completely mass transfer controlled reaction ($p_i = O$), ratio is unity, When the reaction is not at all mass transfer controlled ($P_g - P_i = O$), the ratio is zero. For an intermediate condition, the ratio varies from 0. to 1.0.

(b) *Ruthven's method*: The interphase mass transfer factor has also been calculated with the help of an equation as given by Ruthven[1].

$$\eta' = 1 - \frac{K_o\, d_p^{1.5}}{10.9(Du)^{0.5}},$$

where η' = mass transfer factor,
K_o = apparent rate constant based on unit catalyst pellet volume, sec.$^{-1}$.
d = catalyst particle diam., cm.
D = gas phase diffusivity, cm.^{2}sec.$^{-1}$.
u = linear velocity, cm.sec.$^{-1}$

For negligible mass transfer resistance, η' is almost unity.

(c) Thirdly, the relation of Wheeler[3] has also been used to assess the magnitude; the criterion that mass transfer to the catalyst surface is not affecting the rate is that

$$K/K_{exp} \geqslant 10,$$

where, K = the first order rate constant (sec.$^{-1}$) for an infinitely active catalyst where reaction is completely mass transfer controlled and K_{exp} = experimentally observed rate constant (sec.$^{-1}$). K is given by,

$$K = 10 \times \sqrt{u/Md^3P},$$

where
u = linear velocity, cm.sec.$^{-1}$,
M = mol. wt. of the feed,
d = catalyst particle diam., cm.,
P = pressure, atm.

The values of $(P_g - P_i)/P_g$, η' and K/K_{exp} are given in Tables 1 and 2 for two typical cases with wide variations in mass velocity, catalyst bed height and L/D ratios.

Discussion

It was observed that in all cases and at all temperatures, the % conversion decreased with increase in gas flow rate. A typical sequence has been given in Fig. 1. Further, at the highest working temperature of 220°C and with space velocity of 2000 (wt gas, hr^{-1}), the % conversion in all the five sets of experiments remained almost the same—the highest and the lowest being 78 and 75 respectively. From this first hand examination of conversion, it appears that interphase mass transfer resistance is not significant. Had the resistance been appreciable, the % conversion would have differed by a wider margin.

As has been noted, the value of $(P_g - P_i)/P_g$ is zero, when interphase mass transfer resistance is eliminated. As a matter of fact, it is very difficult to realise this value in laboratory experimentation. The value of $(P_g - P_i)/P_g$

TABLE 1—VARIATION OF COMPARATIVE VALUES OF MASS TRANSFER FACTOR WITH TEMPERATURE

L = Bed ht = 5.0 cm.
D = Reactor diam. = 5.6 cm.
L/D = 0.9709. Catalyst volume = 100 cc.

Reaction Temp, °C	Flow Rate, L/h.	Mass Velocity, g. cm^{-2} hr^{-1}	Rey. No., N_{Re}	Rate Const., hr^{-1}	% Conv.	$\frac{p_g - p_1}{p_g}$	η'	K/K $_{exp}$
160	223.2	4.474	5.437	3.905×10^2	33.13	3.052×10^{-2}	0.9867	86.0
180	226.9	4.346	5.281	1.062×10^3	65.97	6.029×10^{-2}	0.9652	32.82
200	208.3	3.831	4.655	1.384×10^3	78.32	6.866×10^{-2}	0.9581	24.50
220	255.9	4.506	5.475	1.706×10^3	78.43	7.226×10^{-2}	0.9542	22.48

TABLE 2—VARIATION OF COMPARATIVE VALUES OF MASS TRANSFER FACTOR WITH TEMPERATURE

L = 19.0 cm. D = 2.55 cm.
L/D = 7.452 Catalyst volume = 100 c. c.

Reaction Temp., °C	Flow Rate, L/h.	Mass Velocity, g. cm.$^{-2}$ hr^{-1}	Rey. No., N_{Re}	Rate Const., hr^{-1}	% Conv.	$\frac{p_g - p_1}{p_g}$	η'	K/K_{exp}
160	336.2	25.61	31.12	2.837×10^2	17.66	0.8034×10^{-2}	0.9960	410.2
180	334.8	24.32	29.54	5.276×10^2	32.50	1.425×10^{-2}	0.9927	110.2
200	318.5	21.32	25.91	1.536×10^3	67.05	2.847×10^{-2}	0.9830	88.14
220	315.4	21.99	26.71	1.737×10^3	71.86	3.034×10^{-2}	0.9806	84.32

is chosen where in practice, mass transfer factor can be neglected and the choice is limited by the accuracy with which kinetic experimentations are conducted. Thus, Yang and Hougen[7] noted that for an experimental accuracy of 10 per cent in the reaction rate measurements, mass transfer resistance can be neglected if $(P_g - P_i)/P_g$ is 0.1 or less; for 5 per cent accuracy, it is 0.05 or less and so on. The values of $(P_g - P_i)/P_g$, given in the tables and in the plots, range from 0.5×10^{-2} to 7.2×10^{-2}. Accepting the above reasonings, it can be said that even the highest value of 0.072 reflect a condition where for practical purposes interphase mass transfer resistance can be neglected. It is observed that values $(P_g - P_i)/P_g$ increase with increase in temperature (Fig. 2), but decrease with increase in gas flow rate. The tables include minimum gas flow rate for the temperature given; this flow rate was gradually increased to about four times this minimum value and the corresponding decrease in

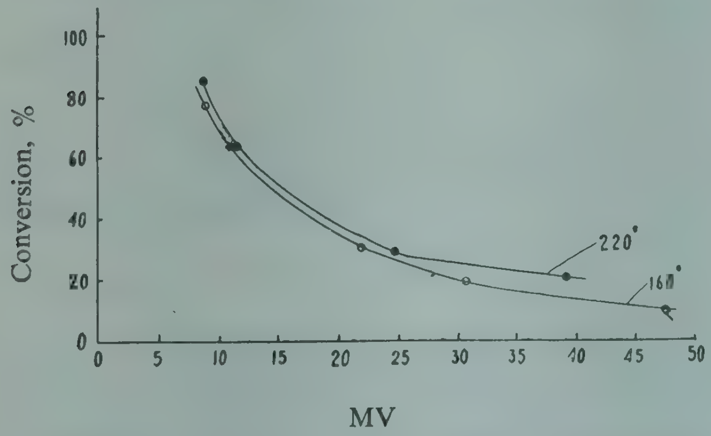

Fig. 1—Variation of Conversion with Mass Velocity
L=Height of the bed 10 cm.
L/D=3.92

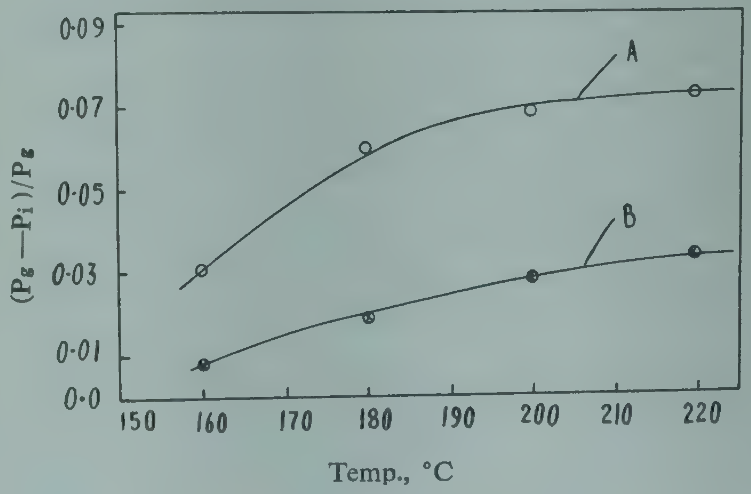

Fig. 2—Variation of $(p_g - p_1)/P_g$ with Temperature and L/D Ratios

A—Ht. of the bed=5 cm.
L/D=0.9709
MV =4.8 g.cm.$^{-2}$ hr^{-1}

B—Ht. of the bed=19 cm.
L/D=7.45
MV =24.5 g.cm.$^{-2}$ hr^{-1}

$(P_g - P_i)/P_g$ was noticed in all cases. It can also be observed from Fig. 3 that an inverse proportionality exists between $(P_g - P_i)/P_g$ and η'—the more the value of the former the less the value of the latter and *vice versa*.

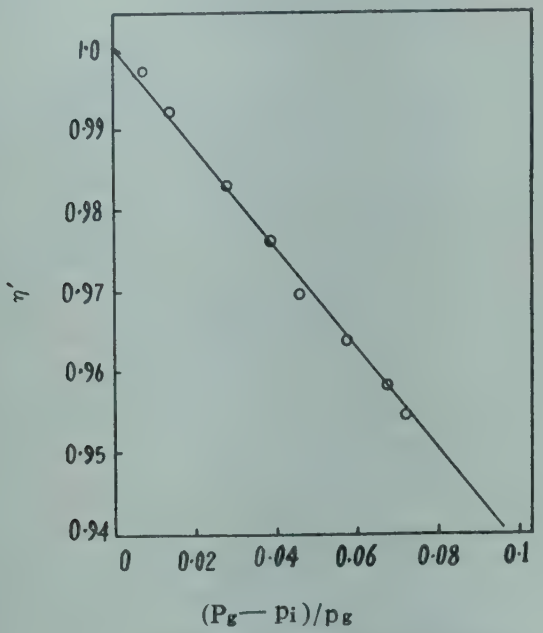

Fig. 3—Variation η' with $(p_g - p_i)/p_g$

Particle Size and Mass Transfer Factor: It was observed that the values of $(P_g - P_i)/P_g$ for 3×6 mm. catalyst particles were almost identical with those for 6×6 mm. catalyst particles with respect to flow rate and temperature. For example, at 160°C, with flow rate of 13.6 L/hr/cc of catalyst, the $(P_g - P_i)/P_g$ for 6×6 mm. catalyst particles was 0.4067×10^{-2}, as compared to 0.4581×10^{-2} for 3×6 mm. catalyst particles. Practical difference in mass transfer rates for different particle sizes did not, therefore, exist for the present case.

Ratio of Bed Length (*L*) *to Reactor Diameter* (*D*) *and Mass Transfer Factor*: Five L/D values for as many bed lengths in two reactors were available. In the reactor of 2.55 cm. diameter three bed heights were used so that linear velocity is different in each bed for a fixed space velocity. At the reaction temperature of 220°C with space velocity of 2000 hr^{-1}, the values of $(P_g - P_i)/P_g$ and per cent conversion, given below, show how the former decrease with bed height, i.e. with increase in linear velocity. Since the contact time is the same, the per cent conversion remains almost identical irrespective of linear velocities in the above cases. The importance of linear velocity lies only in eliminating the resistance to external mass transfer. When external mass transfer is not limiting, for a given contact time, increase in linear velocity (also an increase of L/D) does not reflect in greater conversion.

Bed height, cm.	$(P_g - P_i)/P_g$	Conversion, %
6.0	0.078	77.0
10.0	0.057	75.0
19.0	0.039	78.0

Two similar bed heights of 10 cm. were used in reactors of diameters 2.55 and 5.6 cm. This makes L/D of 3.9 and 1.8 respectively. For a given space velocity, the linear velocity will be identical in both the cases. It is seen that at the reaction temperature of 220°C and space velocity of 2000 hr^{-1}, the values of $(P_g - P_i)/P_g$ and % conversion remains identical in both cases; at the space velocity of 5000 hr^{-1}, the same trend exists, the corresponding values are 0.030 and 37 per cent for L/D of 1.8 and 0.034 and 40 per cent for L/D of 3.9. This shows that when external mass transfer is not limiting, the values of $(P_g - P_i)/P_g$ and per cent conversion remains identical, irrespective of reactor diameter, provided linear velocities and contact time remain the same.

Conclusion

From the results, it can be said that under the experimental conditions studied, water gas shift reaction on low-temperature copper oxide-zinc oxide catalyst is not controlled by external mass transfer. It is also observed that laboratory reactors can be used for obtaining activity data without being affected by external mass resistance. Regarding other problem of accounting for the effect of intrapellet and energy transfer processes, these are being thoroughly investigated in the authors' laboratory, the results of which will be published shortly. If all these can be correctly ascertained with the help of laboratory reactors, the trouble for scaling up to pilot plant may not be worth taking and for such cases, the commercial performance of catalysts can be predicted in terms of results obtainable from laboratory reactor.

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[Original mss. received on March 15, 1973]

UDC 541.128+546.74+546.621

In a coprecipitated nickel-alumina reformation catalyst, grinding does not appear to improve the availability of nickel atoms for gas chemisorption. Its chemisorptive capacity rather declines, if the catalyst is ground for longer periods. This has been attributed to a process of thermal sintering. The catalyst cured at higher temperature loses about 90 per cent of its original chemisorptive capacity. A regularity in the decrease in metal area is observed in isothermal sintering of the catalyst, which follows a second order reaction mechanism.

Changes in the State of Metal Dispersion Due to Grinding and Curing in a Nickel Oxide-Alumina Reformation Catalyst

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Introduction

In an earlier publication[1], results were presented on the changes in the physico-chemical properties of nickel oxide-alumina reformation catalyst when subjected to mechanical and thermal treatments. It was shown that the changes which occurred on grinding the catalyst were primarily of subdivision of larger particles resulting in an increase in the surface area, apparent density and the formation of new pores, and beyond a certain grinding period (65 hours) a secondary process of agglomeration caused the reversal of the acquired physical properties. The latter changes were compared with those taking place when the catalyst samples were heated at elevated temperatures. In view of the interesting changes observed, it was decided to extend our studies to the changes, if any, in the state of metal dispersion due to grinding or curing. In the present study, hydrogen chemisorption has been utilized for the measurement of metal surface areas of the ground or cured samples. The Kinetics of sintering has also been studied and it has been found to be a second order reaction.

Experimental

Preparation of the Samples: Three series of samples were prepared. The preparation of samples of series A and B has already been described[1], which included the ground and cured samples. For the preparation of series C samples, the catalyst was heated in a muffle furnace in air at 800°C and about 100 g. of samples were taken out at 0, 4, 8, 22, 46 and 70 hours.

Gases: Hydrogen was used for the reduction of the catalysts and chemisorption studies. Helium was used for dead space measurements. Hydrogen, obtained from M/s. Indian Oxygen Ltd., was purified by passing through a 'Deoxo' tube to remove any trace amount of oxygen. The water formed was then removed by passing the gas in successive towers of silica gel and magnesium perchlorate. Spectroscopically pure helium was used for dead space determinations.

Hydrogen Chemisorption: The apparatus used for the chemisorption measurement was a conventional all glass apparatus. Samples of each of the catalyst were evacuated at 400°C for a short time. It was then reduced by passing purified hydrogen through the bed of the catalyst at this temperature. A 16 hours treatment with hydrogen was found to be adequate for the complete reduction of the catalyst. To ensure complete reduction of the catalyst, the adsorption of hydrogen for a fixed time was repeated in situ at the reduction temperature until the adsorption was reproducible. The reduced samples were then degassed for several hours at 450°C to 10^{-5} mm. of Hg. and the degassed sample equilibrated with hydrogen for 2 hours at room temperature and at a hydrogen vapour pressure of 100 mm. Hg. The chemisorbed gas was obtained by toeplering out the adsorbed gas to 1-2 mm. pressure. The difference between the adsorbed and toeplered out volume gave the amount of gas chemisorbed on the surface. The chemisorbed hydrogen at a vapour pressure of 100 mm. Hg. was taken to correspond to a monolayer volume.

The nickel metal area was calculated[2] on the basis that each nickel atom adsorbs one hydrogen atom and that each hydrogen atom occupies 6.5 Å^2 of the surface. The hydrogen adsorption at room temperature on α-alumina support was observed to be to the extent of only 0.015 cc/g. This has been taken as negligible for the present study and as such no correction has been made for the amount of gas adsorbed on the support.

Results

The results of the hydrogen chemisorption studies on ground and cured samples are summarized in Tables 1 and 2 respectively. Table 3 contains the isothermal changes in the chemisorption data of the catalyst, when it is treated at 800°C for varying periods. In the columns 2 and 5 are given the total nickel present in the catalyst and the surface nickel accessible for gas chemisorption. Surface nickel has been calculated by employing the relationship[8]:

$$\text{Surface nickel/g. of catalyst} = Ni_s = \frac{2V \times 58.7}{2.24 \times 10^4},$$

where V is the volume of hydrogen gas chemisorbed. In columns 4 and 6 are given the values of metal surface areas in terms of m^2/g of the catalyst and m^2/g of Ni metal, while column 7 contains the chemisorption capacity of each sample. Crystallite sizes determined from the adsorption data are given in column 8 of the Tables 1

TABLE 1—CHEMISORPTION DATA OF GROUND SAMPLES

Grinding Period, hr	Ni. Content, g. g. cat.	Hydrogen Chemisorbed, cc/g. cat	Ni. Metal Area, m²/g. cat.	Surface Nickel, g.Ni./g.cat.	Ni. metal area, m²/g. Ni.	Specific Adsorption Capacity, cc/g.Ni.	Ni. Metal Crystallite Size, Å	Hydrogen Atom Adsorbed/Ni Atom
16	0.076	1.13	3.96	0.00592	52.1	14.87	129.3	0.0778
65	0.076	1.10	3.84	0.00576	50.5	14.47	133.4	0.0758
150	0.076	1.13	3.94	0.00592	51.8	14.48	130.1	0.0778
250	0.076	0.99	3.45	0.00518	45.4	13.02	148.5	0.0682

TABLE 2—CHEMISORPTION DATA OF HEAT TREATED SAMPLES

Curing Temp., °C	Ni. Content, g. g. cat.	Hydrogen Chemisorbed, cc/g.cat.	Ni. Metal Area, m²/g. cat.	Surface Ni., g. Ni g.cat	Ni. Metal Area, m²/g. Ni.	Specific Adsorption Cap., cc/g. Ni.	Ni. Metal Crystallite Size, Å	Hydrogen Atom Adsorbed/ Ni. Atom
450	0.076	1.13	3.96	0.00592	52.1	14.87	129.3	0.0778
550	0.076	0.87	3.05	0.00455	40.1	11.45	168.1	0.0597
650	0.076	0.43	1.50	0.00225	19.7	5.66	342.2	0.02998
750	0.076	0.32	1.10	0.00167	14.4	4.21	468.1	0.0220
850	0.076	0.12	0.43	0.00063	5.6	1.57	1203.8	0.0082
950	0.076	0.11	0.41	0.00057	5.4	1.44	1248.4	0.0075

TABLE 3—CHEMISORPTION DATA OF THE SAMPLES HEATED AT 800°C

Duration of Heat Treatment, hr.	Ni. Content, g. g. cat.	Hydrogen Chemisorbed, cc/g.cat.	Nickel Metal Area, m²/g.Ni.	Surface Nickel, g.Ni/g.cat.	Specific Adsorption Capacity, cc/g. Ni.	Nickel Metal Crystallite Size, Å
0	0.076	0.197	9.1	0.00102	2.59	740.8
4	0.076	0.16	7.5	0.00083	2.1	898.8
8	0.076	0.15	6.9	0.00078	1.97	977.0
22	0.076	0.095	4.3	0.00049	1.25	1567.7
46	0.076	0.08	3.7	0.00041	1.05	1822.0
70	0.076	0.064	2.9	0.00033	0.84	2324.6

and 2. Assuming that the crystallites are of spherical shape, nickel metal crystallite diameter has been calculated from the relation:[4]

$$d = \frac{6}{\rho S \times 10^4},$$

where d is the crystallite diameter in cm, ρ the nickel density and S nickel area in m²/g of nickel. The number of hydrogen atoms adsorbed per nickel atom are shown in column 9 (Tables 1 and 2)

Kinetics of Sintering: The kinetics of sintering of samples heated at 800°C for varying periods have also been studied. The general equations[6] for the first and second order reactions with respect to decrease in the metal surface area due to sintering are respectively:

First order : $lnS = lnSo - Kt$

Second order : $\frac{1}{S} = \frac{1}{So} + Kt,$

where K is the sintering rate constant, S the nickel metal surface area and t sintering time. The nickel metal area values (Table 3) are fitted in the above equations. Figs. 1 and 2 show the graphical representation of the first and second order reactions. It can be concluded that sintering mechanism in reformation catalyst is of the second order. Hermann et al[5] and Maat and Moscou[6] have established sintering to be a second order reaction in the case of platinum on alumina catalyst.

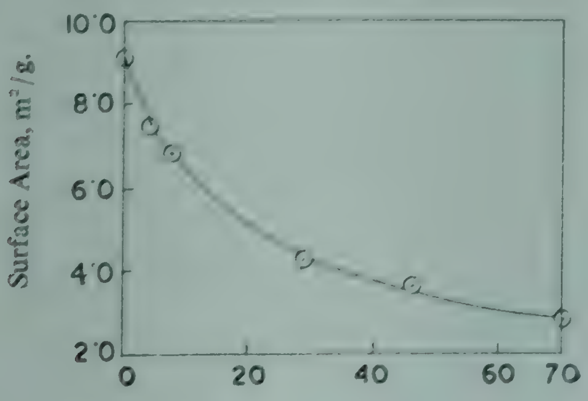

Fig. 1 First Order Sintering Reaction

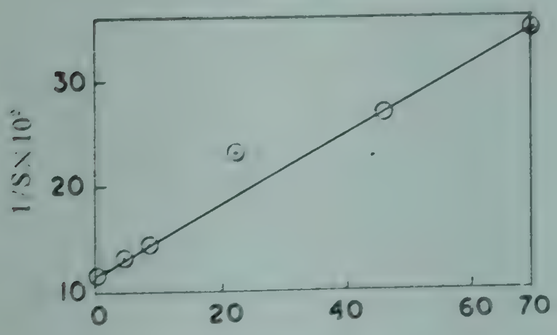

Fig. 2—Second Order Sintering Reaction

Discussion

It can be observed from Table 1 that only a small amount of nickel (8 per cent) in the catalyst is available for gas chemisorption and it remains practically unchanged throughout the grinding. Up to a period of 150 hours grinding there appears to be no change in the nickel metal area and the specific adsorption capacity of the catalyst. The crystallite sizes also remain practically the same. Since there appears to be no change in the state of metal dispersion, it can be concluded that the changes observed previously[1] as regards the surface area, etc., may be due to the changes in the alumina support only and not due to any change in the metal state. Schrader et al[7–9] have reported that milling of nickel-silica catalyst and nickel powder leads to a change in the lattice defects of the solid. This should then reflect in a change in the active sites and thereby in the chemisorptive capacity of the catalyst. But in this study no change in the chemisorptive capacity of the catalyst up to a grinding period of 150 hours has been found. This may be due to the fact that in the present case the catalyst samples were ground for 16 hours and above, whereas in Schrader et al's work the maximum period of grinding has been only 140 min. It has also been reported[9] that following an initial increase the lattice disorder decreases with time. However, beyond the grinding period of 150 hours (at 250 hours), a reduction in the metal surface area as also in the available surface metal and adsorption capacity of the catalyst is observed. Further studies are required to draw definite conclusions, the above change is indicative of the phenomenon of sintering taking place if the catalysts are ground for longer periods. This sintering is believed to be caused due to frictional heat evolved in the ball mill[10]. It can thus be inferred that not only the attempts to increase the chemisorptive capacity of reformation catalysts by grinding is futile, but if ground for longer periods, a process of loss in metal area occurs.

It can be seen from Table 2 that on increasing the temperature of curing beyond 450°C, the phenomenon of sintering takes place. With the advancement of sintering, there is a gradual reduction in the nickel area and the nickel available for chemisorption goes down from 8 per cent in the sample cured at 450°C to 0.75 per cent in the sample cured at 950°C. Consequent on this, the adsorption capacity and the total metal surface area also decreases, there being about 90 per cent loss in the chemisorptive capacity of the catalyst from 450 to 950°C. This loss in the chemisorptive capacity of the catalyst is accompanied by an increase in the nickel crystallite sizes. The growth in the nickel crystallite size is almost tenfold in the sample sintered at 950°C. Furthermore, the catalyst cured at 450°C shows chemisorptive power of 0.0778 atom of hydrogen/nickel atom. This indicates that nickel is not very well dispersed on the alumina support as compared to platinum in the case of platinum on alumina catalyst, where every platinum atom is in an exposed surface and H/Pt ratio is of the order of 0.99[11]. With the increase in curing temperature the hydrogen to nickel atom ratio declines indicating a decrease in the availability of nickel atom for chemisorption. The nickel crystallites, as measured with hydrogen chemisorption, show a considerable growth followed by loss of nickel surface area. A regularity in the decrease of nickel metal area is observed when the catalyst is sintered at 800°C for varying periods (Table 3). The sintering of nickel alumina reformation catalyst has been shown to be a second order reaction (Fig. 2) which is explained as indicating a second order dependence of rate of removal of nickel from dispersed phase to a crystalline or condensed phase.

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[Original mss. received on June 6, 1972

UDC 541.128+546.74+546.621:542.46

The effect of aging on a nickel oxide alumina type naphtha reformation catalyst in an industrial reformer has been investigated. The surface area, pore size distribution, mechanical strength and activity of the catalyst discharged from different types of reformer tubes have been compared with those of the fresh catalyst. The catalyst recovery and activity are found to be dependent on the mechanical strength and pore size distribution respectively. The changes in surface area and mechanical strength have been explained in the light of sintering of the catalyst.

Performance of a Catalyst in a Reformer With Aging —A Case Study

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A gas mixture, suitable for methanol synthesis, is produced by catalytic reformation of naphtha or refinery gas in presence of steam. Theoretical considerations suggest that the reformed gas, used for this purpose, should contain a low level of methane and a comparatively higher concentration of carbon dioxide. Hence, from kinetic considerations, it is required that the reformer is to be operated under the conditions of high steam carbon ratio (6.0 and above), low liquid space velocity (0.5—0.6 kg/lit. of cat/hr) and high exit temperature in the range of 850-880°C for the production of reformed gas containing less than 1 per cent methane. As a consequence of high operating temperature, the catalyst bed is subjected to severe thermal stress, the effect of which may manifest in the loss of surface, shrinkage of pellet, depletion of active component from the catalyst and the other related properties. In spite of the fact that the catalyst functions with a high steam-carbon ratio and low liquid space velocity the deterioration of a catalyst is fast under such thermal conditions particularly where the short reformer tubes are used. The decline in efficiency is reflected in appearance of 'hot spots', 'hot tube' and giraffing, followed by increased methane slip, dusting and gradual increase in pressure drop.

In a reformer where there are a large number of tubes in one assembly, the observed decline in efficiency presents the average picture. It is not possible to assess the change in condition of the catalyst bed and its efficiency in individual tubes. It would be quite interesting to study the physico-chemical changes that might have been caused by the defect in design of a reformer and correlate this with its activity which may help to improve the catalyst formulation for efficient performance under such conditions.

An extensive study has been carried out in bench scale units and pilot plants by different workers[1–3]. But a more elaborate study is necessary for quantitative assessment of the catalyst deterioration in the light of the problems encountered in a commercial plant with the aging of the catalyst. Hence, in the present work, the authors have made an attempt to investigate the changes in the physico-chemical properties, which the catalyst suffers under drastic operating conditions and correlate these properties with the decline in catalytic activity. The results of such investigations will help in formulating a catalyst which can withstand the extreme condition associated with a reformer having short tubes and high tube-skin temperature.

Plant Condition

A commercial reformer, installed for the production of methanol synthesis gas, was charged with a co-precipitated alumina base nickel catalyst. The catalyst was charged in the form of 10×10 mm. cylindrical tablets. The reformer comprises 176 tubes of 10 feet length arranged in four assembly. In each assembly there are 44 vertical tubes arranged in two rows. Each row of tubes is heated from the sides by two sets of burners (each set consisting of eleven burners).

After the completion of reduction when the reformer was loaded, it was observed that the initial period of operation was quite satisfactory and the tube skin temperature, pressure drop, methane slip were all within the design limits. But with the advancement of time, the plant started facing some problems, such as the formation of hot and patchy tubes, the skin temperatures of which were in the neighbourhood of 1000°C, while those of the other tubes were in the range 960-975°C. The development of this situation was followed by the appearance of carbon and catalyst dust in the condensate, and increase in methane slip and reformer pressure drop. The deterioration of the catalyst progressively enhanced with the period of operation. After 2160 hours of run, it was found that the plant reached the permissible operational limits and the shut down for replacement of the catalyst was unavoidable.

After cooling the reformer and opening the tube heads, the catalyst beds presented an interesting picture. In some of the tubes, catalyst beds retained their original height, irrespective of their skin temperature. On the other hand, in some other tubes catalyst bed heights were appreciably reduced. Other important observations were that at the inlet side catalyst pellets of all the tubes were coated with carbonaceous materials and the amounts of recovered catalyst were not equal for all the tubes and extent of recovery does not have any relation with skin temperature of the tubes.

It was not possible to check the condition of the catalyst in the reformer tubes individually *in situ* and the reformed gas at the outlet gave the average composition contributed by all the tubes in an assembly of 44 tubes. Hence, it was decided to study the physico-chemical properties of the discharged catalyst from some selected tubes to get a comparative and meaningful information in relevance to reformer conditions.

For a systematic study, the tubes were classified into four categories on the basis of thermal conditions and depression of catalyst bed heights, viz. (A) normal tube with low depression of catalyst bed height, tube skin temperature in the range 960-975°C; (B) normal tube with high depression of catalyst bed height, tube skin temperature in the range of 960-975°C; (C) hot tube with low depression of catalyst bed height, tube skin temperature in the neighbourhood of 1000°C; and (D) hot tube with high depression of catalyst bed height, tube skin temperature in the neighbourhood of 1000°C.

Operating Parameters and Plant Details

Reformer pressure : 12 kg/cm^2
Liquid space velocity : 0.3—0.4 kg/lit./hr
Steam/Naphtha ratio : 9—12
Recycle gas flow : 10% of the reformed gas
Inlet temperature : 425—450°C
Outlet temperature : 850—880°C

Reformer Pressure Drop, kg/cm^2

Initial stage 0.4—0.6
Before complete shutdown 1.2—1.4

Methane Slip at the Outlet, %

Initial stage 0.01—0.05
Before complete shutdown 0.8—1.2

Catalyst Recovery, %

From the tube A : 80
,, ,, ,, B : 60
,, ,, ,, C : 86
,, ,, ,, D : 68

Experimental

All the samples were tested for surface area, porosity, mechanical strength and phase composition. Experimental methods adopted in their measurements are discussed briefly in the following lines:

(*a*) *Surface area*: The surface area of each sample was determined by the classical BET method using nitrogen as adsorbate at −195°C.

(*b*) *Total pore volume and pore size distribution*: Total pore volume was determined by the difference of helium and mercury displacement values. The pore size distribution was measured in a mercury porosimeter having a working range up to 5000 psi.

(*c*) *Mechanical Strength*: The mechanical strength of the tablets was determined in a Hounsfield tensometer. The average of ten tablets was computed as the crushing strength of the sample under experiment.

(*d*) *Phases*: The phase composition of both fresh and used catalysts was determined by x-ray diffraction technique.

The activities of the catalysts, fresh and used, were tested similarly in an experimental set up described in an earlier work[4] and the experiments were carried out under the following conditions: L.H.S.V. = 0.8; steam/carbon ratio = 6.0; outlet temperature = 850°C; pressure = Atmospheric.

Discussion and Conclusion

In the present paper, the changes in the physico-chemical characteristics of the catalysts, selected from different groups of tubes, were investigated and the residual activities of these catalysts measured in a bench scale unit and compared with the original catalyst. Attempts have been made to identify the causes of deterioration of the catalysts and correlate them with the reformer performance. The progressive deterioration of the reforming efficiency, as observed in the case study, must be the resultant effect of changes in physical and chemical nature of the catalysts caused by thermal imbalance as well as distribution pattern of the feed. At the same time it cannot be ruled out that the thermal imbalance and feed distribution might have been caused by changes in the packing nature, in flow restriction, void formation in the bed and channelling. Hence, it is worth while examining the physical changes which have occurred after 2160 hours of run of the catalyst in the plant.

Surface area, porosity and pore size distribution of the discharged catalyst are presented in Table 1; side by side data on the fresh catalyst are also included for getting a comparative picture. It might be observed that there is a remarkable change in the structural and textural parameters of the catalysts in all the categories of the tubes. There is a high drop in surface area from 48 to 2.47-3.94 m^2/g. The difference in the temperature of the tubes or their packing height as observed after shutdown does not have any relation to the extent of reduction of surface. The almost identical drop in surface area in all tubes under different skin conditions does not appear to to be abnormal; because reduction of surface area is related to the phenomenon of sintering, rate of which is regulated by temperature of the bed. In addition to bed temperature, the composition of the gaseous atmosphere to which the bed is subjected may influence the rate of sintering. Sintering of alumina starts above 900°C in presence of air but it is faster at higher temperature[6]. It is quite possible that the rate of sintering in the tube with lower skin temperature was comparatively slow at the normal tube temperature (950-960°C) but the slow rate of sintering has been fully compensated in the long period of operation and after 2160 hours the extent of sintering equalled that in the hot tubes and ultimately catalysts in all the tubes irrespective of tube condition attained nearly identical surface.

Loss of surface may be due to another reason. It has been observed[5] that presence of γ-Al_2O_3 contributes to the development of larger surface. It may be seen from Table 2 that the fresh catalyst contained γ-Al_2O_3 which completely disappeared in discharged catalyst. The loss of γ-Al_2O_3 from the system must have contributed, at least partly, in the reduction of surface area.

Porosity and pore size distribution of the spent catalyst present a notable feature (Table 1). Porosity of the samples remained practically unchanged under prolonged use of the catalyst in plant. The difference in value from sample to sample is only marginal which is of minor significance. But when the porosity is examined along with pore size distribution, the picture becomes quite interesting and significant. Pore size distribution pattern of the used catalyst is widely different from that of the fresh catalyst. In the fresh catalyst 70 per cent of the pores are below 500 Å whereas in the used catalyst pore size up to 500 Å accounts for only 5-30 per cent. When compared among different groups, it may be observed that catalysts in the hot tubes suffer more in losing finer pores compared to normal tubes. The fact that the pore volume remains unchanged and only the distribution of the pore spectrum shifted from the finer structure to wider pore region leads us to believe that larger pores are created by the collapse of the pore wall between smaller pores. As a result pore volume remains unchanged though proportion of the wider pores has increased.

TABLE 1—SURFACE AREA AND PORE SIZE DISTRIBUTION

Sample	Surface Area, m^2/g.	Pore Volume		Pore Size Distribution, % by volume				
		cc/g.	cc./100 cc.	4-175, Å	175-300, Å	300-400, Å	400-500, Å	500-75000 Å
Fresh	48.0	0.2441	49.4	49.1	12.0	3.2	2.3	33.4
A	2.47	0.2556	51.6	26.6	1.3	1.3	0.6	70.2
B	3.94	0.2493	51.0	15.7	3.2	2.5	3.2	75.4
C	2.23	0.2420	49.6	1.7	1.1	1.1	1.7	94.4
D	2.63	0.2502	51.0	0.6	3.0	2.4	2.4	91.6

The mechanical strength of the catalysts is presented in Fig. 1. This value for different groups increased by 50-100 per cent over that of the fresh catalyst. Strength of the catalyst generally increases with increase of curing temperature, because at higher temperature extent of sintering will be more. On the basis of this observation it may be expected that the catalyst tablets discharged from the hot tubes should have been proportionally stronger. On the contrary, one finds that the mechanical strength of the tablets is equally affected both in hot and normal tubes. But the strength of the pellets is comparatively less in tubes where there was appreciable depression in bed heights. This observation is well corroborated by the amount of recovery of whole pellets from different tubes. Higher depression is accompanied with lower mechanical strength and greater loss of fines (Fig. 1).

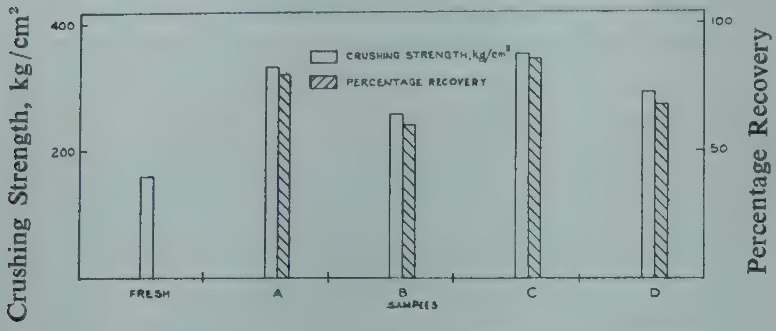

Fig. 1—Comparison of Crushing Strength and Recovery of Catalyst

The catalysts were examined for nickel content and phase composition. There is no loss of nickel from the system. In some of the samples nickel percentage shows a slightly higher figure than in the fresh catalyst. This may be accounted if we look to the phase composition. In the used catalyst, the major fraction of nickel is present as metallic nickel. When estimated as such, nickel percentage is likely to be slightly higher in used catalyst than that of the fresh catalyst.

The fresh catalyst comprised alumina support and nickel oxide. In the support there are two forms of alumina, the major fraction being α-alumina. In the used catalyst γ-variety has completely transformed to α-type. Formation of $NiAl_2O_4$ spinel is a noticeable feature. Its presence in the oxidized catalyst may account for gradual deactivation of the catalyst through the formation of alumina spinel which may be difficult to reduce in presence of high concentration of steam. This aspect is being studied separately, in this laboratory. The presence of metallic nickel in the used catalyst shows incomplete oxidation before cooling the reformer.

The decline in activity of the catalysts varies from tube to tube. Fall in the activity is more for catalysts of the hot tubes than for those of the normal tubes. Methane slip with fresh catalyst is less than 1.0 (Fig. 2) whereas the leakage for the used catalyst varies from 1.4 to 5.6 per cent. For normal tubes they are 1.4 and 2.2 per cent and these for hot tubes 5.6 and 3.8 per cent. Fall in activity does not bear any proportionality with porosity or surface area. However, an explanation can be drawn on the basis of the pore size distribution. Here again, the results prove that though the surface area and porosity are complementary in character, porosity must be considered as separate and independent catalytic parameter. It may be seen that with greater percentage of finer pores activity is higher although the surface area and porosity are similar. The maximum decline in activity (Sample C) is associated with lowest percentage of fine pores (0.6 per cent). This relationship is presented in Fig. 2.

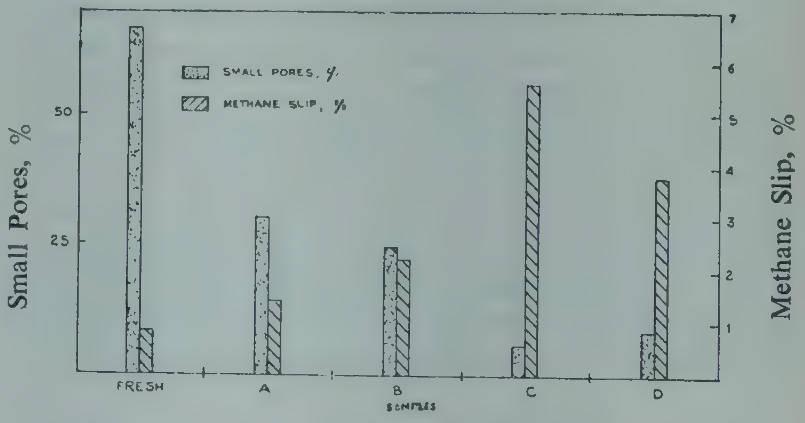

Fig. 2—Comparison of Methane Slip and Percentage Small Pores

TABLE 2—PHASE COMPOSITION AND NICKEL CONTENT

Sample	% Ni	Phases
Fresh	11.63	α-Al_2O_3, γ-Al_2O_3, NiO
A	11.98	α-Al_2O_3, Ni, NiO, Traces of $NiAl_2O_4$
B	11.79	α-Al_2O_3, Ni, NiO, Traces of $NiAl_2O_4$
C	12.05	α-Al_2O_3, Ni, NiO, Traces of $NiAl_2O_4$
D	11.86	α-Al_2O_3, Ni, NiO, Traces of $NiAl_2O_4$

From the foregoing discussions our observations may be summarised as below:

1. Sintering of the catalyst in a reformer under study is a predominant phenomenon.

2. Reduction of surface due to sintering along with phase transformation is considerable. The catalysts lost more than 90 per cent of their surface irrespective of tube conditions during period of operation.

3. Mechanical strength of pellets increased in all tubes. Dusting loss was found more where the increase of strength was comparatively less and depression in bed is greater.

4. There is no nickel loss from the system.

5. γ-phase present in fresh catalyst completely transformed into α-phase and a new phase of $NiAl_2O_4$ spinel appeared in the system.

6. Activity of the catalyst has declined more in tubes of high skin temperature compared to normal tubes.

7. Activity of the catalysts appears to be related with finer pores rather than with surface area and porosity.

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[Original mss. received on March 16, 1973]

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UDC 631.812.12: 532.13: 632.12

The angle of repose is widely used in assessing the flowability of granular materials. In the present study, the angle of repose of various granular fertilizers with varying moisture content was determined. The results reveal that some of the fertilizers are more moisture-sensitive than others. The moisture sensitiveness of a fertilizer appears to depend not only on its chemical composition but also its granulometry. The effects of various other parameters that affect the flow properties of granular fertilizers are discussed.

Effect of Moisture on the Flow Characteristics of Granular Fertilizers

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The study of the flow properties[1-5] of granular fertilizers is important in the design of silos, bunkers, bins and other storage equipments. A dry granular fertilizer is free-flowing but when it is moist on account of absorption of moisture from the atmosphere or due to the retained process moisture, it may lose its free-flowing characteristics and create difficulties in the handling of the product. Absorption of moisture from the humid air, during short exposures that occur when moisture-proof bags are opened, increases the cohesiveness of the particles of fertilizer, causing considerable inconvenience during its distribution in the field. It has been found, as the present experiments indicate, that the moisture tolerance with respect to its drillability or flow characteristics varies widely from fertilizer to fertilizer and its determination is of considerable significance, particularly when the fertilizer is to be used under adverse climatic conditions. The flow characteristic of powders or granular materials is quantitatively expressed in the form of angle of repose, which is the angle of elevation of a conical shaped heap, when the material just begins to slide upon itself; conical shaped heaps are formed when the material is allowed to fall freely from a certain height over a horizontal base, the angle so measured is called the static angle of repose. Another angle, 1-5° smaller[2] than the static angle but measured under conditions of dynamic equilibrium, is known as the kinetic angle of repose. In the present study, discussions are limited to the static angle of repose.

The angle of repose, θ, is an indirect measure of internal friction, μ, between the granules.

$$\mu = \tan \theta$$

Fowler and Chodziesner[6] have studied the flow characteristics of wheat, rice, rape seed and sugar, etc. on an wooden chute and developed statistically the following equation for predicting the angle of friction, θ, of dry granular materials.

$$\tan \theta = \frac{a}{f_s^2} + b \frac{(\epsilon)^{0.5}}{D} - cS + d \qquad \ldots \text{(i)}$$

where a, b, c and d are numerical constants and f_s, ϵ, D and S are shape factor, roughness of the surface, diameter and specific gravity of the granules respectively. The term angle of friction is synonymous[6] with the angle of repose.

Fowler and Wyatt[7] studied the effect of moisture on the angle of repose of wheat, sand, polythene chips, millet, rape seed etc., and deduced the following equation for the calculation of the angle, θ:

$$\tan \theta = an^2 + b\,(M/d_{av}) - cs + d \qquad \ldots \text{(ii)}$$

where a, b, c and d are numerical constants, n, M, d_{av}, s are shape factor, moisture content, average particle size and specific gravity of the granules respectively. Fowler concluded that the angle of repose increases with the increase in moisture content of the product, but the above equation does not hold good for millet and rape seed as the moisture is absorbed inside the particles and therefore the effect of moisture is not apparent.

In the present investigation, the flow properties of various granular fertilizers under dry and moist conditions have been studied.

Experimental

As already reported, the flow properties of granular materials are quantitatively measured in terms of the angle of repose. Several methods have been reported in the literature[8–11] for the determination of the same, such as funnel, cylinder, revolving drum, and tilting plate methods, etc. In the present study, cylinder method has been chosen, as it is most accurate, quick and convenient. The principle underlying this method is to measure height (h) and radius (r) of the conical shaped heap and calculate the angle (θ) from the following relationship:

$$\tan \theta = \frac{h}{r} \qquad \ldots \text{(iii)}$$

A hollow open-ended cylinder of about 3″ height and 2″ diam. was taken and placed over a sheet of paper on a fixed horizontal platform; the cylinder was filled to the top with the fertilizer sample and then gradually raised, granules began to flow and a uniform conical-shaped heap formed. The height of the heap was determined with the help of a cathetometer and the diam. by marking four points opposite to each other on the paper along the periphery of the heap and measuring the distances between the opposite points; half of these two average distances gives radius (r) of the heap and the angle (θ) is calculated from equation (iii). A similar experiment was repeated with fertilizer samples of different moisture contents. Fertilizer samples of different moisture contents were obtained by exposing them to 100 per cent R.H. in a desiccator at room temperature and then stored in a corked flask for 16-20 hours so that moisture gets evenly distributed in the granules. The results are within an experimental error of ± 1.5°.

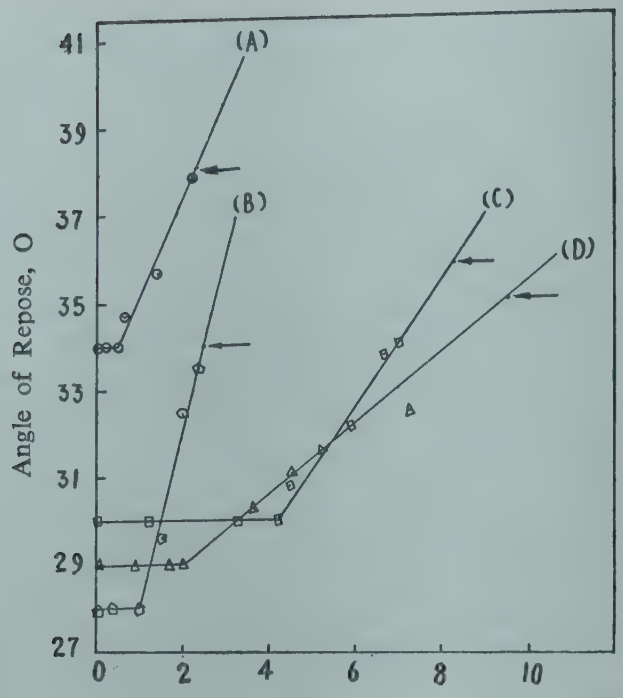
Results and Discussion

The results of angle of repose determination of various granular fertilizers under dry and moist conditions are presented in Table 1 and Fig. 1 respectively. Each result is an average of five to six determinations. The angles of repose of dry granular fertilizers, viz. urea, ammonium nitrate prills, calcium ammonium nitrate (CAN), di-ammonium phosphate (DAP), Suphala (nitrophosphate), double salt (ammonium sulphate-nitrate) and granulated single superphosphate (SSP) are 24°, 27°, 28°, 29°, 30°, 34° and 37° respectively. The appreciable difference in the values of the angles between those of urea, ammonium nitrate prills, CAN, DAP on the one hand and double salt and granulated SSP appears largely due to shape rugosity and roughness of the granular surface. Fertilizers

TABLE 1—ANGLE OF REPOSE OF DRY GRANULAR FERTILIZERS

Fertilizers		Size, mesh (BSS)	Shape of the Granules	Angle of Repose, θ°	True Density, g./cc.	C.R.H., % at 30°C
Urea Prills, 46 % N.		−8+16	Very smooth, spherical	24.0	1.24	72.5
Ammonium Nitrate Prills, 34.5 % N.		−8+16	Smooth, spherical	27.0	1.43	59.4
Calcium Ammonium Nitrate, 25 % N.		−5+ 8	Smooth, nearly spherical	28.0	1.62	58.1
{ Limestone	28% }					
{ Ammonium Nitrate	72% }					
Di-ammonium Phosphate	18-46-0	−8+16	Nearly spherical	29.0	1.61	82.8
Nitrophosphate (Suphala)	15-15-15	−6+10	Nearly spherical	30.0	1.82	45.0
(Ammonium Nitrate	39.5 %					
Ammonium Phosphates	7.5 ,,					
Di-calcium Phosphate	17.2 ,,					
Potassium Chloride	24.0 ,,					
Calcium Sulphate	3.7 ,,					
Impurities (<1%)	8.1. ,,)					
Double Salt (Ammonium Sulphate-nitrate)	26%N.	−5+16	Irregular, rough	34.0	1.58	62.3
{ Ammonium Nitrate	40% }					
{ Ammonium sulphate	60% }					
Ganulated SSP, 19.7% P_2O_5		−5+ 8	Irregular, rough	37.0	2.00	85.0

Parentheses indicate the chemical analysis of the fertilizer.



Moisture, %

Fig. 1—A=Double Salt, B=CAN, C=Suphala, D=DAP
←Very Cohesive no flow

under the first category, i.e. urea, ammonium nitrate, etc., on their physical examination have been found to be smooth and nearly spherical in shape. It has been observed that smooth and spherical shaped particles encounter less resistance during flow as the number of inter-particle contacts and friction is minimum and thus have a lower angle, whereas double salt and granulated SSP, on account of their irregular shape and rough surface, have more inter-particle contacts and friction, encounter more resistance during flow and have higher values of the angle.

Apart from shape rugosity and roughness, density is another factor which affects the flow of granular materials. Particles of greater density do not cohere with other particles and roll down along the heap during flow. The denser particles are free-flowing and non-cohesive whereas less dense particles (powder) are non-free-flowing and cohesive. The data on the true density of various fertilizer granules are recorded in Table 1. Granulated SSP having a density 2.00 g/cc. has an angle of repose 37°, which is contrary to the expected pattern. The higher value of the angle for SSP is evident from its irregular shape and roughness of the granular surface, which offsets the effect of density. This behaviour can be very well seen from equation (ii); as there is a square of shape factor (n) in the equation, so a small variation in shape will offset the effect of density. The effect of density is well marked in the case of fertilizers having smooth surface and spherical shape, e.g. Suphala, CAN and DAP, etc.

Effect of Moisture: The effect of moisture on the flow characteristic of urea and ammonium nitrate prills could not be studied as these fertilizers, being relatively non-porous ceased to be free-flowing even with 0.6 per cent moisture and the heaps formed gave erratic values of angles of repose. For free-flowing ammonium nitrate and urea prills, the moisture content should be less than 0.5 per cent. Other fertilizers, however, gave consistent results with higher moisture contents. Fig. 1 shows the plot of angle of repose versus moisture content of different fertilizers. The nature of curves (Fig. 1) suggests that at lower moisture level there is no increase in the angle of repose but afterwards it increases progressively with increase in moisture content. This may be interpreted as follows: the flat portion of the curves gives an indication of the moisture-holding capacity of the granules with respect to the liquid phase generated by absorption of moisture, which is held inside the pores of the granules and therefore the surface characteristics remain unaltered; when more moisture is added, the saturated solution formed gets distributed also on the surface of the granules which increases their cohesiveness and there is an abrupt increase in angle of repose. The nature of slope (Fig. 1) would largely depend on the increase in solution phase with increasing moisture content as well the extent to which solution phase appears on the granular surface, the former would depend on the solubility of the fertilizer salt and the latter on the composition and granulometry of the fertilizer.

In the case of CAN there is no increase in the angle of repose up to 1 per cent moisture content, after which there is a sharp rise in the angle as the moisture content is increased, and at moisture level 2.5 per cent and above the granules become very cohesive as indicated by an arrow in Fig. 1 and no flow has been observed. Limestone, which constitutes about 28 per cent (Table 1) of the total composition of the granule, appears to increase the moisture-holding capacity of the granules and thus makes it less susceptible to moisture than ammonium nitrate prills.

No increase in the angle of repose has been observed up to 0.5 per cent moisture in the case of double salt, afterwards it increases with increase in moisture content and at moisture level 2.35 per cent and above, granules become very much cohesive. The sharp rise in the angle of repose above 0.5 per cent moisture is likely as the chemical constituents consist entirely of ammonium sulphate and ammonium nitrate (Table 1), and increase in moisture produces a large volume of solution phase, which increases the cohesiveness of the granules.

In the case of DAP there is no increase in the angle of repose up to 2 per cent moisture content, afterwards it increases with the gradual increase in moisture content, and at moisture level 9.5 per cent and above, granules become very cohesive and no flow is observed. A comparison of the curves A, B and D (Fig. 1) suggests that the increase in the angle with increase in moisture content is much less for DAP than for double salt and CAN for a similar increase in moisture content. This may be attributed primarily to the low solubility of diammonium phosphate as compared to the ammonium nitrate containing fertilizers. The angle of repose of Suphala is constant up to 4.2 per cent moisture, after which it increases with the gradual increase in moisture content and at 8.3 per cent moisture level the granules become very sticky. The high moisture-holding capacity of Suphala is thus clearly evident and may be due to the composition of insoluble components, many of which are formed during the processing of the fertilizer.

Table 2 indicates the angle of repose of granulated SSP at different moisture levels. As can be seen from the table there is no appreciable increase in the angle between dry and moist SSP samples. The good flow behaviour of SSP granules even at high moisture level is evident from its chemical composition. SSP granules contain calcium sulphate, mono-calcium phosphate and small amounts of di- and tri-calcium phosphates, etc. Mono-calcium phosphate, on account of its low solubility and high C.R.H., is not in a position to generate enough volume of liquid phase to moisten the granules and increase their cohesiveness. The results enumerated in Table 2 are of cured SSP samples, containing about 0.5 per cent free phosphoric acid; it is expected that increase in free phosphoric acid content in SSP granules will increase the angle of repose.

TABLE 2—EFFECT OF MOISTURE ON THE ANGLE OF REPOSE OF GRANULATED SSP

Moisture Content, %	Angle of Repose, $\theta°$
0	37.0
6.4	37.3
7.6	37.5
9.4	38.2
11.1	38.3

Conclusion

The results show that moisture-holding capacity of fertilizers vary from one fertilizer to another and is not dependent solely on the hygroscopic nature of the salt.

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[Original mss. received on March 8, 1973]

UDC 546-28—145:545-84—13:546.161

The geometry and chemistry of the surface of pores in silica gel have been found to alter considerably when treated with hydrofluoric acid of various strengths and under different thermal conditions. Bulk density varies from 0.50 to 0.67 g./c.c., pH from 2.8 to 3.1, liquid loading capacity from 17 to 46 per cent and surface area decreases to 23 m^2/g. No catalytic effect has been observed on these modified silicas up to 350°C.

These silicas have also shown a wide variation in their GSC properties for hydrocarbons accompanied by a slow change of activity upon aging. Several GLC properties, including plate efficiencies, for various solutes have been compared from non-polar and polar stationary liquids coated on hydrofluoric acid-silica, salt-thermal silica and Chromosorb W. A considerable support interaction in hydrofluoric acid-silica has been noticed in the retention indices and their temperature coefficients; the effect being opposite to that of salt-thermal silica when Chromosorb W is assumed as inert and standard. However, retention indices of all solutes have been found to vary linearly with column temperature for all the modified silica supports. Regarding suitability for quantitative analysis, hydrofluoric acid-silica has been found to compare favourably with Chromosorb W.

Studies on Physico-Chemical and Gas Chromatographic Properties of Silica Gels Modified with Hydrofluoric Acid

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It has been demonstrated in earlier publications[2–4] that the geometry and chemistry of the surface of silica gels undergo drastic change when they are first coated with salts of some transition metals and then calcined. However, the presence of metals imposes certain limitations on the application of the silica gels in gas chromatography (GC). For example, polar solutes are retained either too long or completely by these silica gels when used as gas-solid chromatographic (GSC) columns. Necessity was, therefore, felt for a method which would modify the physics and chemistry of silica surface without leaving any harmful residue.

The reaction of hydrofluoric acid with silica was applied under milder conditions in this investigation, hoping that the pore surface will be etched, narrower pores will be widened and large and shallow cavities will be generated on the walls of bigger pores. These textural changes accompanied by reduction of surface hydroxyl groups were believed to impart desirable gas chromatographic properties on the silica gels. Additionally, the silica gels, thus modified, were expected to provide better surface for the emerging field of chemically bonded stationary liquids.

Experimental

Indigenous silica gels were first purified as described in an earlier paper[1] and then treated with hydrofluoric-sulphuric acid mixtures of different compositions under various thermal conditions. The silica from each treatment was washed free of sulphate ions with demineralized water and then oven-dried at 200°C for 5 hours followed by sieving before use. The observed loss of weight of silica gel by hydrofluoric acid treatment was below 40 per cent in all cases.

A few physico-chemical properties of the modified silica supports were determined according to procedures already described[1,4,5]. Gas chromatographic properties were determined in an Aerograph 600D Hy-Fi equipment fitted with a flame ionization detector. The mesh-size of supports was 70-100 BSS for all the columns except that of column 15 which was 60-80 BSS. The dimensions of copper tubing were 5′×1/8″ for columns 1-12 and 10′×1/8″ for the rest.

Results and Discussion

(*a*) *Physical Properties*: The silica gels resulting from the treatment of hydrofluoric acid under varying conditions of dilution and thermal history were designated as SF_1, SF_2, etc. in the second column of Table 1, which also shows changes in physical properties, like pH, bulk density and maximum loading capacity for squalane. It may be noted that all the modified silicas are mechanically stronger than the blank and have developed some degree of water-repellent properties. The pH of the hydrofluoric acid treated silicas varied from 2.8 to 3.1, while that of the blank was 4.4, indicating thereby the presence of some free HF and acidic fluorides on the surface.

The wide variation from 0.50 to 0.67 in the bulk density of the treated silicas (compared with 0.59 of the blank) signifies that hydrofluoric acid can bring about a large change in the pore volume of silica gels.

Mention may also be made that the bulk densities of the hydrofluoric acid-treated silicas lie between those of Chromosorb-W and salt-thermal modified silicas. Comparing the supports of columns 3 and 7 of Table 1, it may be inferred that subsequent calcination of bulk density remains more or less constant.

A rough idea of the pore geometry of SF_3 can be had from Table 2, where its retention times for n-hexane and n-heptane relative to n-pentane were compared with

TABLE 1—PHYSICAL AND KEEPING QUALITY PROPERTIES OF HF-MODIFIED SILICAS AND THEIR COMPARISON WITH CHROMOSORB W AND SALT-THERMAL SILICAS

[SF_1 stands for silicas obtained from the first series of treatment with hydrofluoric acid.]

Description of Columns		Properties of Supports		
Number	Designation	Bulk Density, g./c.c.	pH	Liquid Loading Capacity, w/w %
1.	SF_1	0.50	—	34
2.	SF_2	0.51	—	34
3.	SF_3	0.55	2.8	17
4.	SF_4	0.57	2.8	21
5.	SF_5	0.60	2.8	38
6.	SF_6	0.67	3.1	46
7.	SF_3 heated 950°C for 7 hr.	0.57	—	38
8.	SF_3 aging 4 days	—	—	—
9.	SF_3 aging 7 days	—	—	—
10.	SF_3 aging 10 days	—	—	—
11.	SF_4 aging 10 days	—	—	—
12.	SF_4 aging 40 days	—	—	—
13.	SF_3 coated with 10% squalane	—	—	—
14.	Salt-thermal silica coated with 10% squalane	—	—	—
15.	SF_3 coated with 10% XE-60	—	—	—
16.	Chromosorb W coated with 10% XE—60	0.24	8.10	30-45
17.	Salt-thermal silica coated with 10% XE-60	0.61-0.83	6.3-7.5	30

TABLE 2—COMPARATIVE PORE STRUCTURE OF HF-SiO_2, PORASILS AND CHROMOSORB P

Support	Surface Area, m^2/g	Pore Diam., Å	Retention Time Relative to nP = 1.00 (Uncorrected for gas holdup at 100°C)	
			nH	nHp
Porasil A	410[a]	100[b]	2.33	5.93
Porasil C	126[a]	200-400[b]	2.11	4.11
Porasil D	68[a]	400-800[b]	1.59	2.72
Porasil E	15[a]	800-1500[b]	1.25	1.54
Silica gel	375[c]	25[c]	2.58	6.44
Silica gel II lot	320[b]	75-320[b]	2.18	5.25
Silica gel heated 950°C for 7 hr	291[c]	50[c]	2.24	5.12
Silica gel, 12% w/w Cu coated	24[c]	770[c]	1.25	1.67
Silica gel-HF	23[a]	760-1360[d]	1.28	1.64
Chromosorb P	10[a]	1000-20,000[b] 850-1500[d]	1.22	1.53

[a] Calculated from Fig 1A of reference 6

[b] from manufacturers literature

[c] experimentally determined by B.E.T. method

[d] estimated approximately from graphical correlation of surface area and pore diameters.

different chromatographic supports of known surface area and average pore diameter. Considering the fact that the retentive mechanism of electronically symmetric n-paraffins is solely controlled by pore openings, and since SF_3 behaved close to silica gel modified with 12 per cent copper sulphate and porasil-E, it can be inferred[6] that SF_3 has a surface area of 23 m^2/g. and average pore diameter of 760 Å.

(*b*) *Gas-Solid Chromatographic Properties*: The GSC properties of the hydrofluoric acid modified silicas are given in Table 3. None of the supports has eluted acetone at 100°C. The supports SF_2 in columns 1 and 2 respectively are clearly different from the others. For example, they exhibited higher retentions for most of the solutes and eluted benzene but subtracted cyclohexene and chloroform, unlike the other treated supports in Table 3. In fact, SF_1 and SF_2 are much closer in their GSC properties to the parent silica gel, which does not elute cyclohexene and benzene and has comparable retention of 2.58 and 6.44, respectively, for normal hexane and n-heptane relative to n-pentane. In other words, the preparation of SF_1 and SF_2 represents a milder textural and chemical change in contrast to those of the other modified silicas.

A wide variation in GSC properties for polar and non-polar solutes has been observed among the supports denoted by SF_3, SF_4, SF_5 and SF_6 (vide Table 3), as SF_6 is having relatively larger retentions of cyclohexene and benzene. Evidently, a significant difference in the geometry and chemistry to pore surface can be obtained by controlling the variables of HF treatment on silica gel.

The effect of calcination may be noted in column 7 of Table 3, particularly in the reduced retention of cyclohexene and benzene as compared with blank SF_3: the higher retentions for n-hexane, n-heptane and n-octane clearly indicating a shrinkage of the larger pores by sintering.

The effect of aging of the hydrofluoric acid-modified supports may be seen from the GSC properties of columns 8, 9 and 10 of Table 3. The retention of paraffins was not significantly affected by long keeping, which means that the pore size distribution does not undergo much change on aging. On the contrary, the retention for polarizable hydrocarbons, like the olefins and aromatics gradually decreases, indicating thereby, a slow deactivation of the surface hydroxyl groups on keeping. In order to have a lasting and reproducible chromatographic behaviour, these modified supports will obviously need stabilization.

The modified silicas were tested for catalytic activity up to 350°C with various model compounds, especially the hydrocarbons. No catalytic activity was observed in the chromatograms which did not show any spurious peaks.

(*c*) *Comparative GLC Behaviour*: The gas chromatographic properties of a support when coated with a stationary liquid reflect its details of pore geometry and residual surface activity. The distribution of the stationary liquid assumes the pore configuration of the support and as such governs the various band broadening processes, i.e. the efficiency of the column. The mode of molecular interaction of stationary liquid and solute is influenced by residual support activity, which is generally avoided

TABLE 3—COMPARISON OF ELUTION PROPERTIES OF DIFFERENT COLUMNS DESCRIBED IN TABLE 1

	Relative Retention Data Uncorrected for Gas Held-up at 100°C											
Column Nos. Compound	1	2	3	4	5	6	7	8	9	10	11	12
nH	1.77	1.84	1.26	1.24	1.19	1.34	1.50	1.24	1.24	1.19	1.19	1.60
nH_p	3.59	3.60	1.72	1.62	1.52	2.02	2.64	1.64	1.64	1.58	1.57	1.50
Benzene	12.50	12.23	5.00	3.09	3.38	6.09	2.03	3.24	2.88	2.58	3.00	2.27
Hexene-2	5.67	4.90	2.13	2.00	2.14	3.00	2.05	2.04	1.92	1.81	2.00	—
Cyclohexane	1.80	1.84	1.24	1.24	1.23	1.34	1.47	1.24	1.24	1.25	1.19	1.20
2,2,4, Trimethyl pentane	4.62	4.00	1.86	1.76	1.71	2.26	3.58	1.80	1.84	1.74	1.71	1.62
Cyclohexene	No elution	No elution	2.48	2.24	2.28	3.39	1.92	2.32	2.08	2.13	2.14	1.79
Chloroform	—	—	—	1.52	1.38	2.17	1.32	1.44	—	—	—	1.33
Diethyl ether	—	—	—	—	2.28	3.53	—	—	—	—	—	—
nO	—	—	2.58	2.28	2.23	3.4	5.26	2.36	2.28	2.29	2.14	2.25
nP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
nP (Uncorrected retention volume, ml.)	41.1	40.0	8.6	8.6	14.0	13.00	19.1	12.6	13.7	9.0	8.3	12.2

in a good GLC support. However, the residual support activity sometimes imparts additional selectivity in the resolution of certain compounds.

Under this perspective, theoretical plates (n) have been compared in Table 4 for Chromosorb W, salt-thermal silica and HF-SiO_2 each coated with 10 w/w per cent XE-60 and packed in columns of equal dimensions and run under identical experimental conditions. It may be noted that the plate efficiency of hydrofluoric acid-silica is definitely better than that of salt-thermal silicas and is comparable to that of the classical Chromosorb W for all types of solutes. A further sub-division of (n) between the gas and stationary phases would have provided deeper insight into the comparative pore configuration of these supports. Some idea can, however, be had of support structure from the values of effective plate number (N)[7], which has been computed from the total retention time, minus the gas hold-up time and the experimentally observed peak widths. The resultant N values have been found to be much higher in the hydrofluoric acid-silica in comparison with the other supports. This may be taken as an index of entirely different pore structures generated on silica by hydrofluoric acid and by salt-thermal treatment. It has also been found that the rate of generation of n or N is faster in hydrofluoric acid-silica than in salt thermal silica, indicating a faster mass transfer in the former support.

The observed half-widths corresponding to minimum HETP (at an uniform chart speed of 6 cm/min.) given in the last column of Table 4 are much higher in hydrofluoric acid-silica compared to Chromosorb W. Considering the much smaller pore volume of hydrofluoric acid-silica this support has definitely been overloaded with respect to 10 w/w per cent stationary liquid and consequently suffered a loss in plate efficiency compared with Chromosorb-W. Therefore, a proper comparison should be based on the same ratio of the volume of stationary liquid to pore volume on both the supports.

Regarding residual support activity, it has been found that the specific retention volumes of paraffins are comparable in SF_3 and Chromosorb W when coated with 10 w/w per cent XE-60. But solutes containing heteroatoms, like oxygen, were excessively retarded in the hydrofluoric acid-silica. A more sensitive test of support interaction was applied in the results of Table 6 where retention indices (I) of different solutes were compared in SF_3 and Chromosorb W, coated separately with a polar and non-polar stationary liquid. A strong deviation in the I values of all types of solutes can be noted in the squalane (Sq.) columns. This strong support activity of SF_3 could not be suppressed by coating with the polar XE-60, which is evident from a wide disagreement of I values even for saturated hydrocarbons (vide column Nos. 15 and 16 in Table 5.)

An interesting observation has been found in the elution of olefinic and aromatic hydrocarbons from the Sq-SF_3 and the XE-60-SF_3 columns, the former giving higher and the latter lower retention indices than the standard values from the corresponding Chromosorb W column. The support effect on the isoparaffins is rather small for Sq. but significantly strong for XE-60.

The temperature co-efficient of retention index[8] $\frac{dI}{dT}$ given in Table 6 provides a still more sensitive test of support interaction. A remarkable observation was that the I-T linearity propounded by Saha and Mitra[9] was maintained in the GLC columns from hydrofluoric acid-silica and salt-thermal silica in spite of their strong residual support effect. It may be noted that $\frac{dI}{dT}$ values in Sq. were strongly affected by both hydrofluoric acid-

TABLE 4—COMPARATIVE STUDY OF TOTAL AND EFFECTIVE PLATE NUMBERS AND THEIR RATE OF GENERATION FROM HF-SiO_2, SALT THERMAL SILICA AND CHROMOSORB-W[2] COATED WITH 10% XE-60 w/w

Support	Surface Area, m^2/g.	Pore Vol., m^2/g.	Pore Diam., Å	n	N	n/N	N/t, sec.	W 1/2 at H min., cm.
A—Solution-n-nonane								
Chromosorb-W	1-3[b]	2.8	10,000-20,000[b]	2356	491	4.79	2.019	1.20
Salt-thermal silica	24[c]	0.4769	770[c]	2011	981	2.04	2.018	2.55
SiO_2-HF	23[a]	—	760[a]	2580	1391	1.85	2.451	2.56
B—Solute-butylacetate								
Chromosorb-W				2658	877	3.03	4.845	0.83
Salt-thermal silica				2187	1361	1.60	2.853	2.40
SiO_2-HF				2549	1673	1.58	2.158	3.49

For symbols [a], [b] and [c], see Table 3.

TABLE 5—Retention Indices of Various Types of Solutes from Polar and Non-Polar Phases upon HF-SiO$_2$ and Chromosorb.-W as Refined Evidence of Secondary Support Interaction

Solute	Retention Index in			
	Col.No.15 at 80°C	Col.No.16 at 80°C	Col.No.13 at 86°C	Ref. 5 at 86°C
Diethyl ether	648	578	—	—
Disopropyl ether	—	650	—	—
Hexene-2	628	654	616	606
2,2,4 Trimethyl pentane	709	687	689	694
Cyclohexane	650	711	667	672
Cyclohexene	693	757	682	681
2,3,4 Trimethyl pentane	767	766	760	757
2,2,5 Trimethyl hexane	805	778	787	779
Acetone	797	763	—	434
Methanol	—	712	—	—
Ethanol	—	747	—	—
Ethyl Acetate	784	800	—	557
Benzene	743	826	670	649
1-*cis* 2 Dimethyl cyclohexane	325	873	834	841
1-*trans* 2 Dimethyl cyclohexane	787	839	809	813
Propanol	—	851	—	—
Ethyl methyl ketone	866	862	—	—
Toluene	848	928	784	755

TABLE 6—Further Evidence on Support Activity of Modified Silicas from Comparison of Temperature Co-efficients in GLC Columns

Solute	Temperature Co-efficient of Retention Index dI/10°C, from 10 w/w % Squalane		
	HF-modified Silica, SF$_3$	Chromosorb-W	Salt-thermal Silica
Hexene-2	1.00	0.36	—
Cyclohexene	1.60	2.51	—
Benzene	1.40	2.47	3.22
Cyclohexane	2.60	2.30	3.10

silica and salt-thermal silica for the unsaturated hydrocarbons. These support effects, which were observed in the peak shifting and $\frac{dI}{dT}$ values from the XE-60-SF$_3$ column, may be utilized as additional parameters for the characterization in GC peaks.

(*d*) *Quantitative Elution*: The quantitative elution of all the components in a sample is one of the most essential criteria in GLC. In order to test this, a synthetic mixture of polar compounds comprising hexene-2, cyclohexane, benzene, ethyl acetate, 1-trans-2 dimethyl cyclohexane, and ethyl methyl ketone was analysed in XE-60-SF$_3$ and XE-60 Chromosorb W columns. The results from these two columns agreed well for individual components and for total elution, testifying thereby to the suitability of HF treated silica supports for quantitative GLC work.

Conclusion

It has been demonstrated in this work that the physics and chemistry of silica pore surface can be substantially altered by treatment with hydrofluoric acid. A more drastic textural change is likely under high pressure. Provided the reaction variables are controlled and correlated with the concomitant changes of pore configuration, silica gels can be suitably modified for specific GSC, GLC and adsorption properties.

Acknowledgement

The authors thank Dr. A. Sinha for his interest in this work.

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[Original mss. received on Aug. 18, 1972]

UDC 541.486:545.84—13

For the total analysis of a complex sample, like the naphtha, which contains a host of homologues and isomers in widely varying proportions, the efficacy of any single stationary liquid is definitely limited with respect to its power of fractionation, resolution and identification of its components. These deficiencies can be removed by using a pair of stationary liquids, one separating essentially according to vapour pressure and the other predominantly according to the structural differentials of the solute molecules in both the stages of fractionation by preparative GC and subsequent resolution of the fractions by analytical GC. By choosing squalane and tetracyanoethylated pentaerythritol as the two stationary liquids it has been demonstrated that the efficiency of the retention index and its extended concepts, like Δ I, dI/dT, etc., is vastly improved for the identification of hydrocarbon peaks and the interpretation of complex gas chromatograms.

This principle can be easily extended to the qualitative and quantitative analysis of complex samples of all other chemical types, provided the choice of the pair of stationary liquids is proper and the desired retention data of the components are available in them.

A New Approach to the Improved Separation and Identification of Complex Mixtures by Gas Chromatography —Application to Naphtha

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Introduction

The analysis of complex samples for individual components is practically impossible by the conventional techniques. For example, in the carbon number range of 4 to 10 existing in naphtha or gasoline, there are more than hundred hydrocarbons of various structural types, superimposed with the complexity of innumerable homologues and isomers in widely varying proportions. In spite of the spectacular advances of GC during the last fifteen years or so, many problems still remain in the separation and identification of complex mixtures.

Almost all GC schemes for the resolution of complex samples have been based on the use of single stationary liquids, but none of the stationary liquids, known so far, can completely exploit the small existing separation potentials in order to give a total resolution of all the components in naphtha or gasoline. The non-polar stationary liquids, which separate essentially according to vapour pressure, can give the maximum resolution of saturated hydrocarbons, particularly when high efficiency packed or open tubular columns aided by programmed temperature or flow operations are used. The prior fractionation in a preparative GC column followed by analytical separation in a non-polar liquid cannot even resolve multiplets containing hydrocarbons of different structural types. On the other hand, the polar stationary liquids, which essentially separate according to structural differentials, cause adequate resolution of the olefinic and aromatic hydrocarbons at the cost of poor separation of the saturated counterparts. Obviously, the maximum advantage can be had when the fractionation scheme is designed to exploit all the virtues of the two opposite types of stationary liquids. The use of a mixture of these two stationary liquids in the same column is definitely better than that of single stationary liquid of either type, but it is not the ideal combination. The use of multiple stationary liquids by a few earlier workers[1–6] was, however, conceived for comparing the peaks in the chromatograph of the whole sample, with respect to relative retention-times or specific retention volumes for characterization. Recently, Stuckey[7] has used a DC-550 capillary column in series with another 1,2,3 tris cyanoethoxy propane (TCEP) capillary column for the analysis of complex hydrocarbon samples. In Stuckey's scheme, the olefins and aromatic bands were shifted to cause overlapping on the saturated hydrocarbons of higher carbon numbers, overall resolution in the chromatogram showing not much improvement.

Considering the next phase of analytical problems, viz. the identification of peaks and interpretation of chromatograms, the use of two columns (a non-polar and a polar) is most efficient, even to the extent of making GC almost self-sufficient in the analysis of complex samples. The emergence of Kovats' retention index[8] and its recent extensions by Mitra and Saha[9], Tourres and Loewenguth[10], Walraven *et al*[11], Takacs *et al*[12], Ettre[13] and Kaiser[14] represent a great advance in the characterization of peaks in a complex gas chromatogram. In other words, the retention index and its temperature coefficient for a vast number of hydrocarbons are known in squalane (Sq), permitting various effective correlations with structure. Nevertheless, many multiplets are left unresolved in the chromatogram identified from the results of the squalane column only. When sufficient information of I and dI/dT and other relevant GC parameters of hydrocarbons is available in a structure-specific liquid phase the combined knowledge accruing from the double columns will have the capability to correctly and completely identify almost all the component hydrocarbons in naphtha and other petroleum fractions. The same principle of separation and identification based on the combined use of a non-polar and a polar column can be easily extended to complex mixtures, containing other than hydrocarbon homologues.

The object of this paper is to demonstrate the capabilities and potentialities of a GC analysis scheme based on a pair of stationary liquids of opposite polarity, using naphtha by way of illustration. It has been found that the refined identification parameters derived from retention index can be utilized to a fuller extent, when complex samples are first fractionated in one stationary liquid, and then the resultant fractions are again subdivided in a second stationary liquid, using preparative GC for carbon number and structural type separations.

Principle of the Analysis Scheme

Squalane is the obvious choice as a non-selective stationary liquid, primarily because of the availability of reproducible I and dI/dT values in it for a large number of hydrocarbons of all types[10, 15–17]. The second stationary liquid should be so chosen as to give a large difference in the retention indices of compounds over squalane (△I). Experience has shown that stationary liquids containing strong polar functional groups, like the nitriles, selectively retard the retentions of naphthenes, olefins and aromatics. For example, oxidipropionitrile[18] (ODP), tetra-cyanoethylated pentaerythritol[19] (TCEPE) [Mitra, G. D. and Saha, N. C. Personal communication] and TCEP elute benzene after n-decane, which is the most desired criterion in the analysis scheme. Stationary liquids having higher △I values for various chemical types will add to the efficiency of the fractionation and subsequent analysis of a complex mixture. TCEP and TCEPE both have been found to be superior to ODP, because of higher △I values for naphthenes, olefins and aromatics. From available data in literature[20], TCEP seems to satisfy this criterion better than TCEPE. However, TCEPE has been used, TCEP being not available in this laboratory. The fractionation scheme will definitely be most effective when an ideal polar liquid phase having the highest structural specificity is used. Adequate information is, however, lacking in literature about the prediction of a stationary liquid which is highly specific for the retention of a given solute.

The analysis scheme involving preparative GC from a TCEPE column followed by analytical GC of all the fractions in the squalane column under several isothermal conditions is given in Fig. 1. The distribution of hydrocarbon types obtained with the analytical squalane column has been shown for the 600-700 index cut, but the same will also be applicable to other fractions, except the the last one which mainly contains aromatics. The relative distribution of hydrocarbon types in a given fraction as well as from fraction to fraction through a TCEPE column is given in Table 1. The preparative fractionation could be improved by using a non-polar stationary liquid, but the subsequent analytical GC in TCEPE will not be effective, because sufficient and reliable data are not available in this phase at present. However for maximum resolution and individual component identification a double preparative fractionation scheme using squalane followed by TCEP and using I, △I and dI/dT in both the analytical columns will be the most preferred choice. Work along this line is in progress in this laboratory.[21]

Experimental

Two preparative and two analytical columns were used in this work and the details of their preparation and

Fig. 1—Scheme for Naphtha Analysis

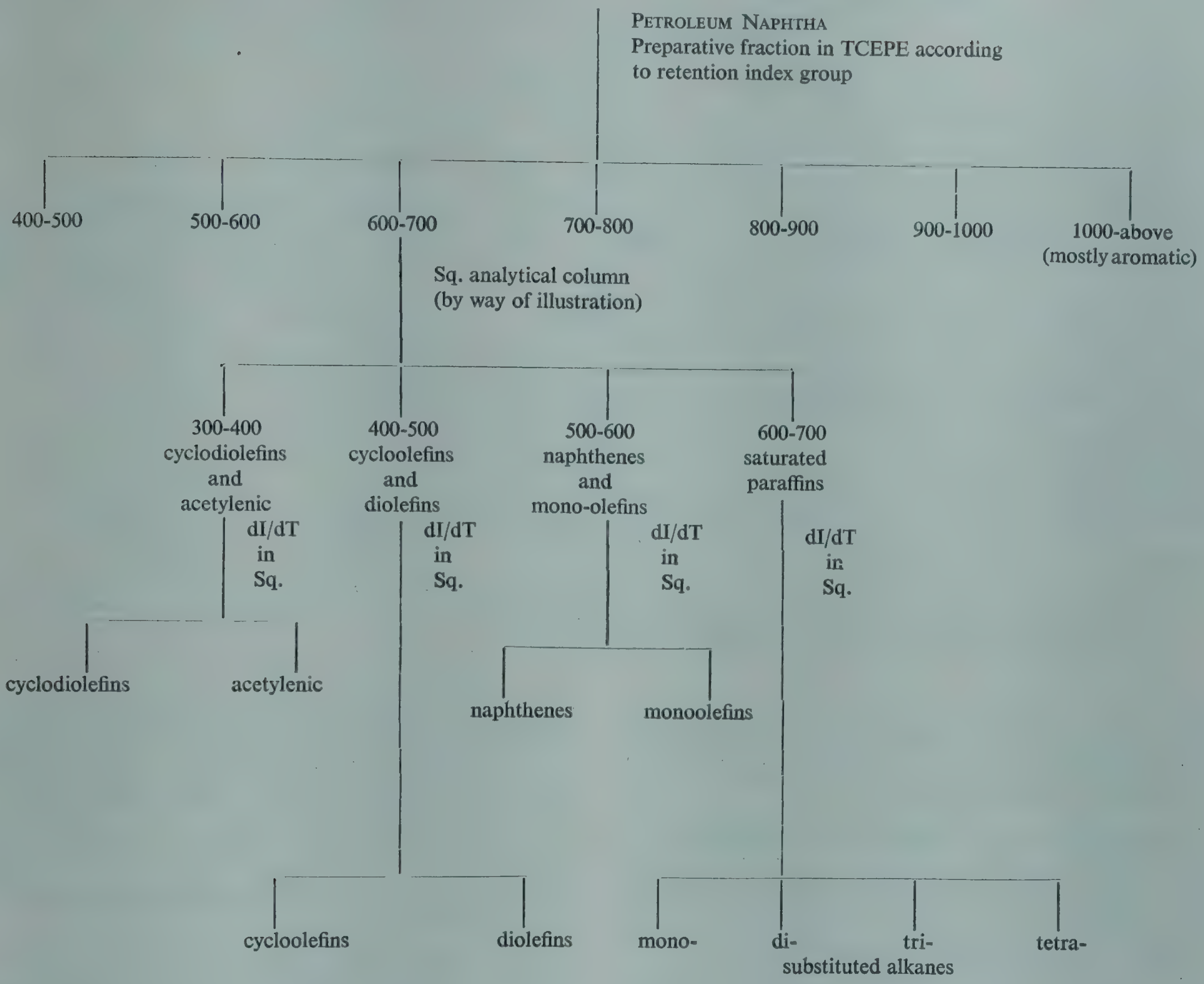
Petroleum Naphtha
Preparative fraction in TCEPE according to retention index group
400-500
500-600
600-700
700-800
800-900
900-1000
1000-above (mostly aromatic)
Sq. analytical column (by way of illustration)
300-400 cyclodiolefins and acetylenic
400-500 cycloolefins and diolefins
500-600 naphthenes and mono-olefins
600-700 saturated paraffins
dI/dT in Sq.
dI/dT in Sq.
dI/dT in Sq.
dI/dT in Sq.
cyclodiolefins
acetylenic
naphthenes
monoolefins
cycloolefins
diolefins
mono-
di-
tri-
tetra-
substituted alkanes

TABLE 1—Range of ΔI Values of Different Types of Hydrocarbons

Type of Hydrocarbons	ΔI ($I^{67}_{\text{TCEPE}}-I^{67}_{\text{Sq.}}$) range
n-paraffins	0-0
Alkyl paraffins	0-5
Cyclo-paraffins	60-100
Mono-olefins	80-130
Cyclo-olefins	150-200
Di-olefins	200-250
Cyclo-diolefins	250-300
Acetylenes	300-350
Aromatics	400-425

operation are given in Table 2. In the preparative PTGC, fractions were collected automatically in the collecting traps provided along with the Autoprep-700, using an ice-bath. In all, seven fractions were collected from a total of five injections of 1 ml. each. The overall collection efficiency was 75 per cent, most of the losses being confined in the first two fractions. The cut points were found out from the increased peak heights of the naphtha sample which was dosed with all the C_6 to C_{13} n-paraffins, after comparing with the chromatogram of the blank naphtha sample under identical conditions of the preparative GC. Fractions 1 and 2 may be collected in n-nonane of known volume to minimize the evaporative and collection losses.

Results

The preparative chromatogram of the naphtha in TCEPE along with the mode of temperature programming

TABLE 2—EXPERIMENTAL CONDITIONS OF THE PREPARATIVE & ANALYTICAL COLUMNS

Column Type	Polar Stationary Liquid		Non-polar Stationary Liquid	
	Analytical	Preparative	Analytical	Preparative
Column dimension	15ft × 1/8 in.	33ft × ¼ in.	20ft × 1/8 in.	30ft × ¼ in.
Liquid phase	TCEPE	TCEPE	Sq.	SE-30
wt. % liquid	21	21	5	20
Solid support	Chrom 'P'	Chrom 'P'	Gas Chrom 'Q'	Chrom 'W'
Mesh size of support BSS	60-80	60-80	60-80	60-80
Carrier gas	N_2	H_2	N_2	H_2
Inlet pressure Psi.	10	28	15	32
Column temp., °C	63/98	60/175	40/50/67/75/86	50-140
Thermal condition	isothermal	PTGC	isothermal	PTGC
Sample injected	0. 1-0.7 μl	1 ml	0. 1-0.2 μl	2 ml
Origin of the liquid phase	Applied Science	Applied Science	BDH	Aerograph
Detector	FID	TC	FID	TC
Detector temp., °C	—	125	—	110
Filament current	—	70 mA	—	80 mA
Collector tip temp., °C	—	ambient	—	Ambient
Instrument model	600 D Aerograph	Autoprep-700 Aerograph	500 D Aerograph	Autoprep-700 Aerograph
Attenuation	*	× 16	**	× 32

*Variable in all fractons in TCEPE as indicated in the chromatograms

**Constant for any fraction, but different for different fractions in Sq.

and fractional cut points are shown in Fig. 2. The same naphtha was also chromatographed in a SE-30 preparative column in order to compare the resolution from the TCEPE column (vide Fig. 3).

All the fractions from TCEPE were chromatographed isothermally at multiple temperatures for obtaining I and dI/dT values in the squalane analytical column. The chromatogram of F_1 in squalane is shown in Fig. 4 as an illustration. The isothermal chromatograms of all the fractions are given from the TCEPE analytical column at different temperatures (Figs. 5 to 11). The retention indices (calculated with the help of the bracketting normal-paraffin peaks present in the chromatograms) were shown against each peak in the chromatograms.

The gas hold-up time corrections were made with separate methane injections as usual[22]. The identification of peaks for all the fractions and quantitative analysis are given in Tables 4-10.

It has been observed that the retention indices of aromatic hydrocarbons from the present squalane column

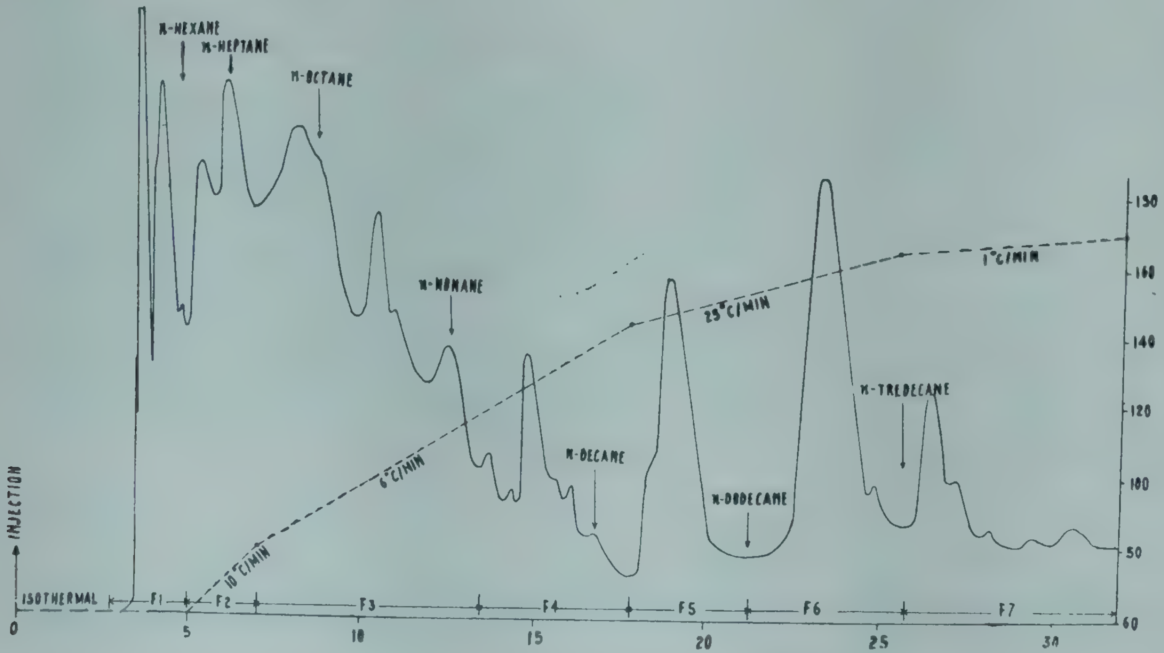

Fig. 2—Chromatogram of a petroleum naphtha from the preparative column, 33′ × ¼;—21% TCEPE on Chromosorb—P, 60/80 mesh, under non-linear Programmed Temperature operation, the chained line giving details of temperature programming.

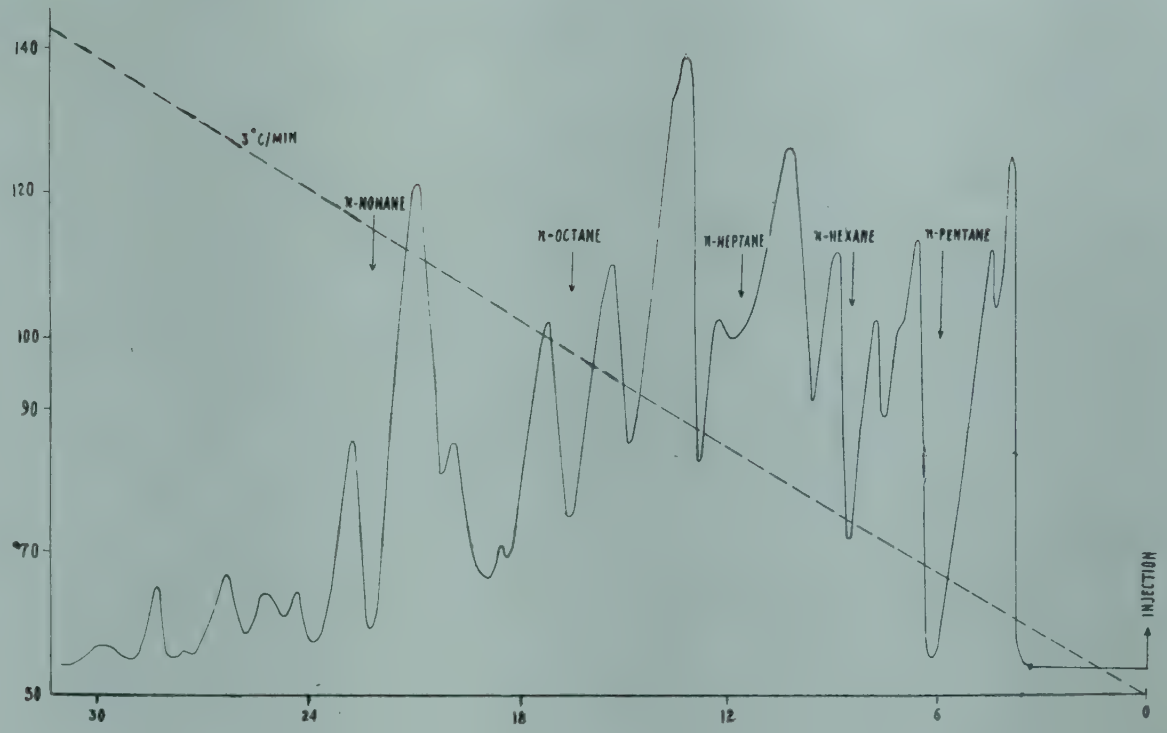

Fig. 3—Chromatogram of the petroleum naphtha from the preparative column, 30′ × ¼″; SE-30 on Chromosorb-W, 60/80 mesh, under linear programmed temperature operation

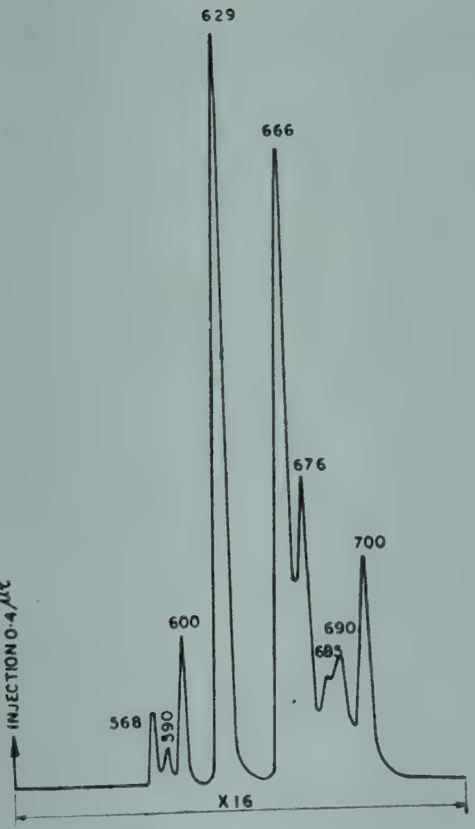

Fig. 4—Analysis of the TCEPE preparative fraction F_2 in the Sq. analytical column at 50°C, the retention indices being given at the top of mesh peak

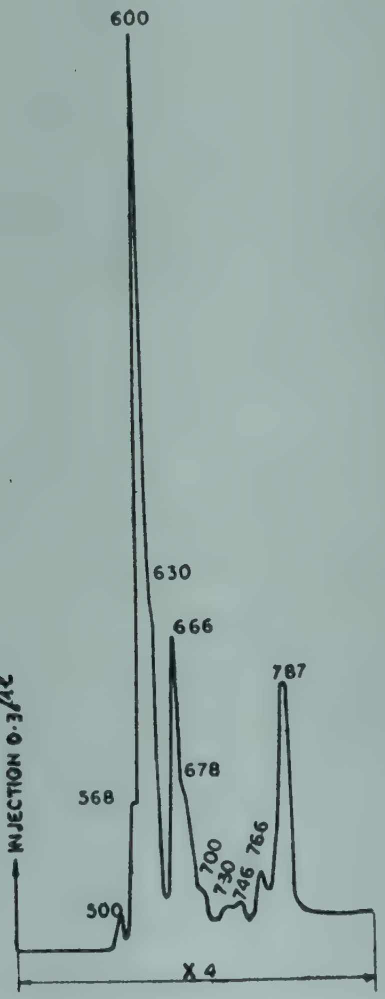

Fig. 5—Chromatogram of the TCEPE preparative fraction F_1 from the TCEPE analytical column at 65°C, the number at the top of each peak denoting retention index

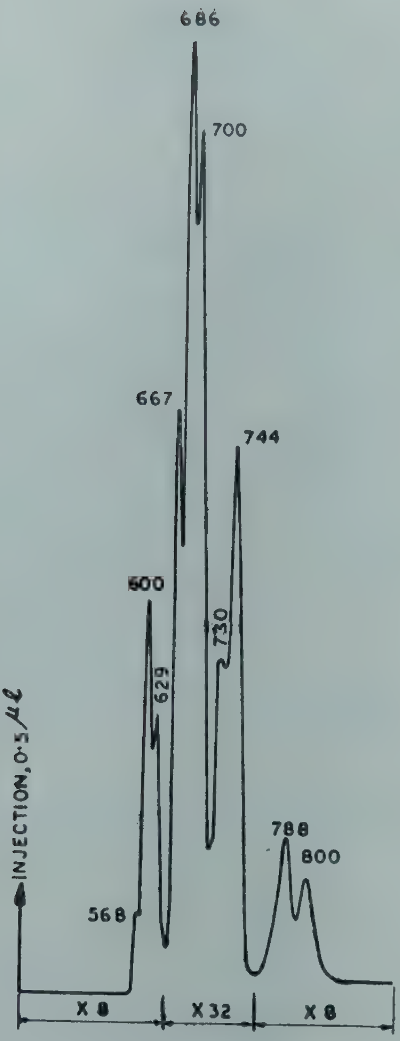

Fig. 6—Chromatogram of the same sample F_2 of Fig. 4 from the TCEPE analytical column at 63°C along with retention index of each peak

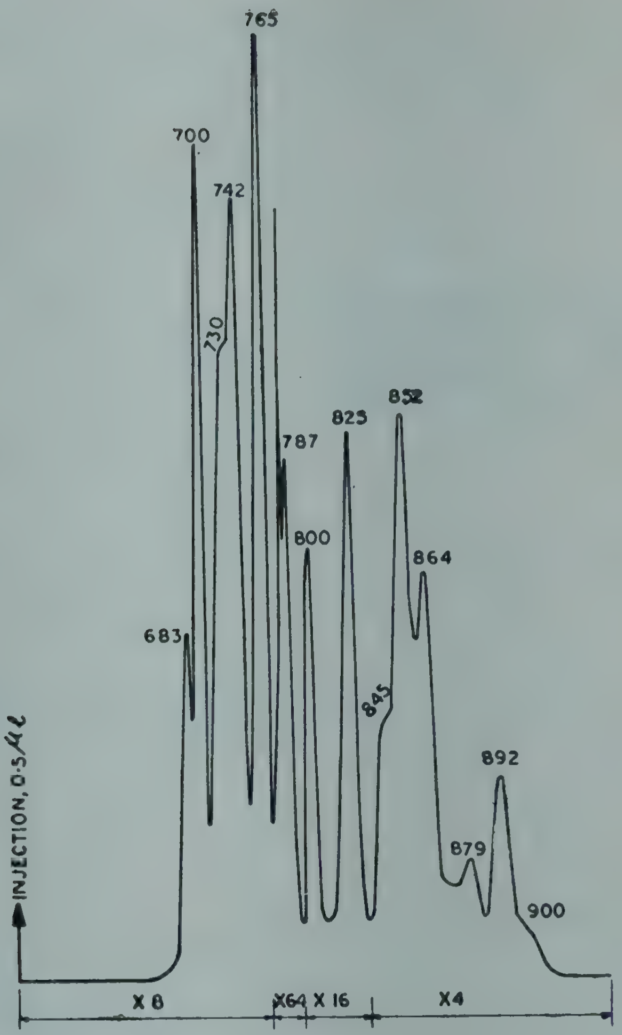

Fig. 7—Analysis of the TCEPE preparative fraction F_3 from the TCEPE analytical column at 63°C, the retention index being shown at the top of each peak

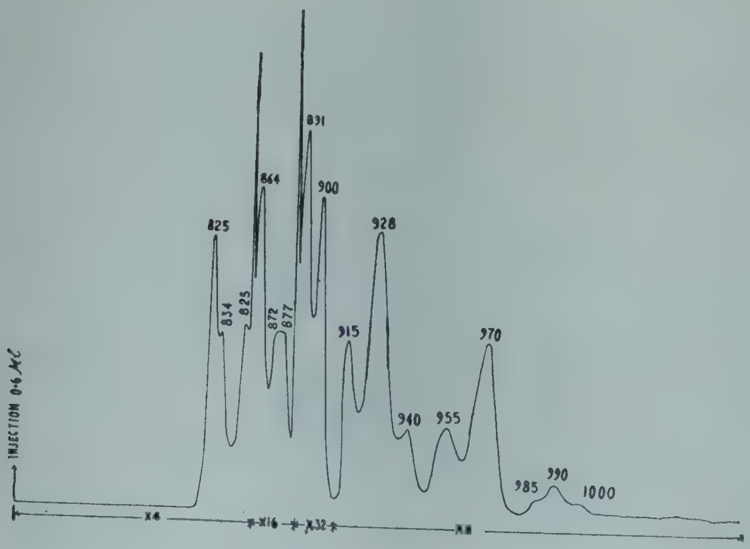

Fig. 8—Analysis of the TCEPE preparative fraction F_4 in the TCEPE analytical column at 63°, the retention index being shown at the top of each peak

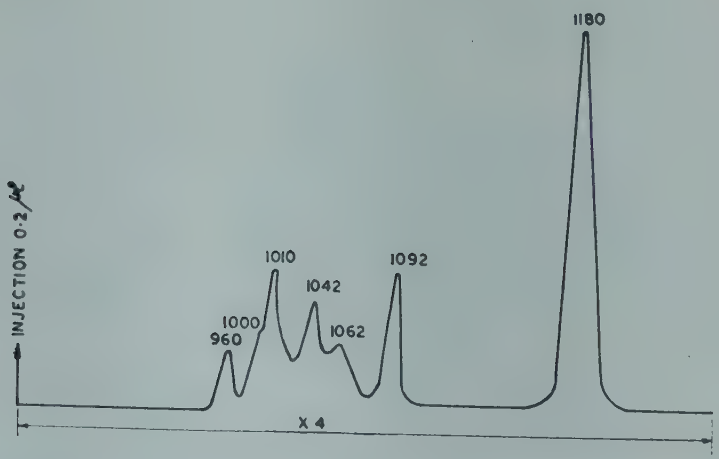

Fig. 9—Chromatogram of the TCEPE preparative fraction F_5 in the TCEPE analytical column at 98°C along with retention index distribution

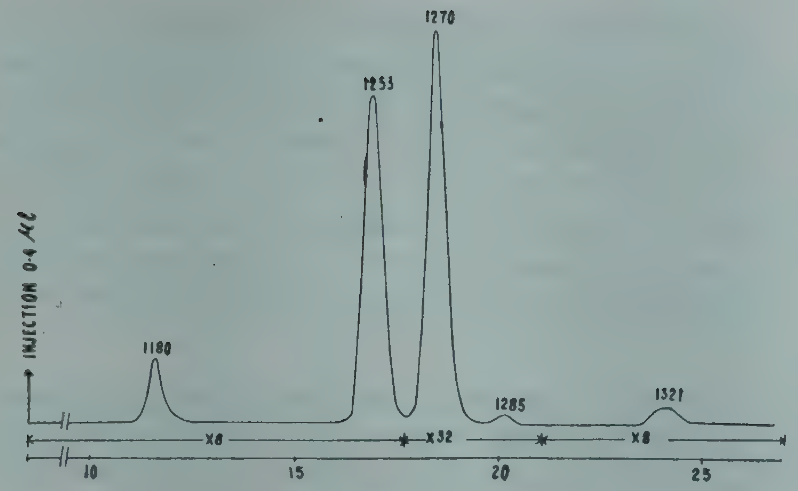

Fig. 10—Analysis of F_6 of Fig. 2 in the TCEPE analytical column at 98°C along with retention index distribution.

are somewhat greater than the corresponding figures in literature[17]. According to Evans and Smith[23] this is due to the oxidation of squalane on keeping for a long time. But the I-values, I-T linearity or dI/dT of alkanes, cyclanes, and olefins were not affected. The aromatic hydrocarbons gave a linear relation of I with T, dI/dT being fairly close to the literature values. Moreover, I values from this squalane column for aromatic hydrocarbons, when plotted against the corresponding literature values, yielded a straight line, thereby providing a calibration method for the inter-conversion of data[24].

Discussion

A critical comparison of the two preparative chromatograms (Figs. 2 and 3), reveals that (i) the spacing between the adjacent n-paraffins is much narrower in TCEPE than in SE-30; this reduced resolution and non-return of the detector signal closer to base line have caused great interfraction overlapping, particularly in the lower hydrocarbon region (Fig. 2); on the contrary, the fraction above n-decane is well resolved and (ii) there is a considerable shift in the distribution of components in the two preparative chromatograms, the whole naphtha

TABLE 3—Abbreviations Used in Tables 4 to 10

Symbol	*Meaning*
M	methyl
m	meta
Pr	propyl/propane
B	butane/butyl
P	pentane/pentyl/penta
p	para
O	octane/octa/octyl
o	ortho
H	hexane/hexa/hexyl
Hp	heptane/hepta/heptyl
n	normal
N	nonane
Bz	benzene
Tol	toluene
Xy	xylene
D	di
T	tri, tetra
t	trans
C	cyclo
c	cis
E	ethyl
CP	cycloparaffin
CO	cyclo-olefin
CDO	cyclo-diolefin
BC	bicyclo compound
MO	mono-olefins
DO	di-olefins

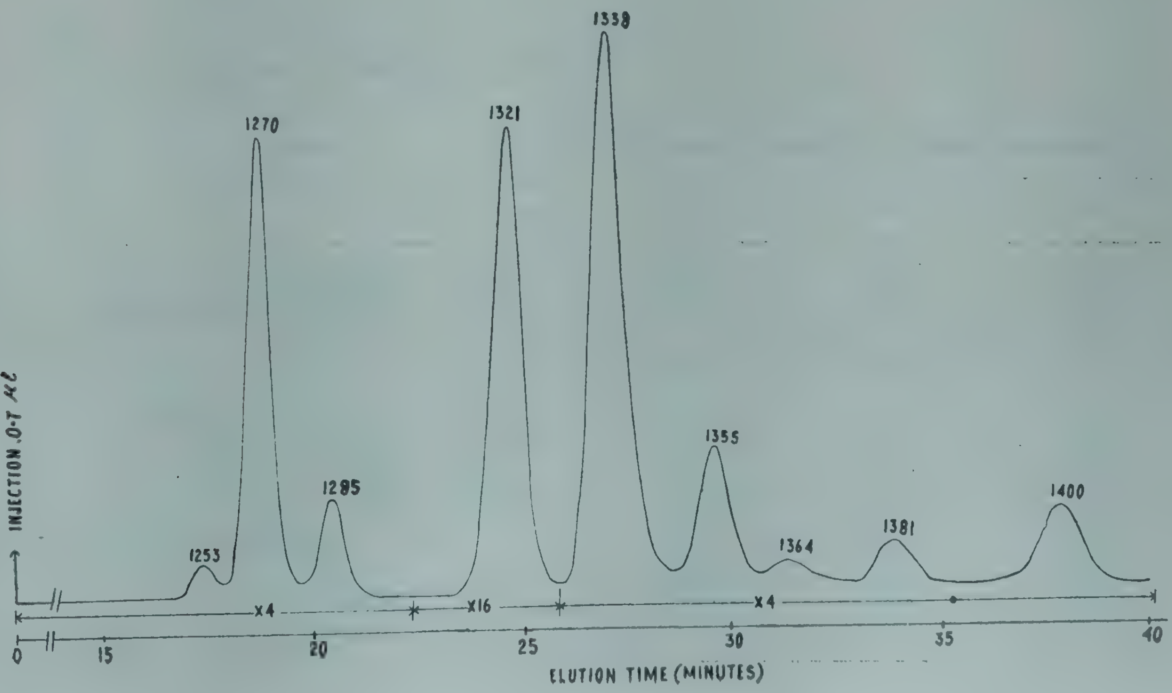

Fig. 11—Analysis of the last fraction F_7 of Fig. 2 in the TCEPE analytical column at 98°C, the retention index being shown at the top of each peak.

being collected before n-decane in SE-30, whereas a large number of compounds eluted after n-decane in TCEPE.

In order to know the component distribution, in general from the TCEPE preparative cut, all these fractions were rechromatographed with an analytical TCEPE column (Figs. 5-11) which provided actual retention index distribution of each fraction. Additionally, these chromatograms provide some valuable information for the identification of peaks in each fraction. These were not available from squalane runs alone as given below:

(a) Retention indices of components in squalane span from 500 to 700 in F_1 as well as F_2. The same two fractions, when re-run in TCEPE, show many peaks with retention index greater than 700, which obviously belong to olefins and naphthenes. The presence of two peaks in F_2 of retention indices 685 and 690 at 50°C in squalane (vide Table 5 and Fig. 4) and their absence in F_1 (Table 4) clearly eliminate the possibility of alkanes being represented by these peaks. Had 3,ethylpentane and 2,2,4, trimethylpentane been present, they would have eluted in F_1 also.

(b) In F_3 (Table 6), at least the peaks having index values between 850 to 900 in squalane at 86°C must belong to saturated hydrocarbons, because the presence of any

TABLE 4—ANALYSIS OF FRACTION 1

Retention Indices at Different Temperatures (°C), Sq.				Tentative Identification	Positive Identification
40	50	67	86		
500	500	500	500	nP, P-2 (t) 2M 1:3B (diene)	nP, P-2 (t) 2M 1:3B (diene)
569	570	572	572	2MP, 23 DMB	2MP, 23 DMB
584	585	586	586	3MP, H-1, 1-H (yne) 1:4H (diene)	3MP, H-1 1:4 H (diene)
600	600	600	600	n-H, 2MP-2, 2M 1:3P (diene), 2E 1:3B (diene)	n-H, 2MP-2
629	630	631	632	24DMP, 4M 1:3P (diene) 2M 1:3P (diene) 33 DMP-1 233 TMB-1	24DMP, 33DMP-1 233 TMB-1
665	666	666	668	2MH, 1:6 Hp (diene)	2 MH
675	676	677	677	3 MH	3 MH
700	700	700	700	nHp, Hp-2 (t) 3MH-2(c)	nHp

TABLE 5—ANALYSIS OF FRACTION 2

Retention Indices at Different Temperatures (°C), Sq.				Tentative Identification	Positive Identification
40	50	67	86		
566	568	570	572	CP, 23 DMB	CP 23 DMB
584	585	586	586	3MP, H-1, 1:4 H (diene) 1-H (yne)	3MP, H-1, 1:4H (diene)
600	600	600	600	nH, 2MP-2, 2M 1:3 P (diene), 2E 1:3B (diene)	nH, 2MP-2
627	629	632	635	MCP, 233 TMB-1	MCP, 233 TMB-1
665	666	668	668	2MH, 1:6 Hp (diene)	2 MH
675	676	677	676	3MH	3MH
683	685	688	—	1 C_3 DMCP, 3EP, 3MH-3 (t)	I C_3DMCP, 3MH-3 (t)
688	690	693	—	1 t_3DMCP, 1 t_2 DMCP, 224 TMP	1 t_3DMCP, 1 t_2DMCP
700	700	700	—	nHP, Hp-2 (t) 3 MH-2 (c)	nHp, Hp-2 (t) 3 MH-2 (c)

TABLE 6—ANALYSIS OF FRACTION 3

Retention Indices at Different Temperature (°C), Sq.				Tentative Identification	Positive Identification	% in the	
50	67	75	86			Fraction	Whole naphtha
1	2	3	4	5	6	7	8
629	632	633	636	MCP, 233TMB-1	MCP, 233 TMB-1	1.30	0.340
664	668	672	672	CH	CH		
675	677	679	—	11 DMCP, 3MH, CH (ene)	11 DMCP, CH (ene)	10.80	2.81
684	687	689	—	1c$_3$DMCP, 2MH-3 (t), 3EP	1c$_3$DMCP, 3MH-3 (t)		
690	694	697	—	1t$_2$DMCP, 1:4CH (diene)	1t$_2$DMCP		
700	700	700	700	nHp, Hp-2 (t), 3MH-2 (c)	Hp-2 (t) 3MH-2 (c), nHp	13.00	3.38
728	732	735	737	MCH, 2233 TMB, Dicyclopropyl methane	MCH, 2233 TMB, Dicylopropyl methane		
735	739	742	—	ECP, MCH (ene-3), MCH (ene-4), 223TMP, 233TMP-1	ECP, MCH (ene-3), 233 TMP-1, MCH (ene-4), 223TMP		
742	745	747	—	methylene cyclohexane, 1t$_2$c$_4$ TMCP, 33DMH	methylene cyclohexane, 1t$_2$c$_4$ TMCP, 33DMH		
749	752	755	757	1t$_2$c$_3$ TMCP	1t$_2$c$_3$ TMCP	33.10	7.61
765	765	766	766	2MHp, 4MHp, 234TMP-2	2MHp, 4MHp, 234TMP-2		
771	772	773	774	3MH*p*, 3EH, 34DMH	3MHp, 3EH, 34DMH	13.00	3.38
787	790	794	—	1Ec$_3$MCP, 1t$_4$DMCH, 1C$_3$-DMCH, 1M1:4 CH (diene)	1Ec$_3$MCP, 1t$_4$ DMCH, 1C$_3$ DMCH		
790	794	797	—	11DMCH, 1Mt$_2$ECP, 1Et$_3$-MCP, 1Et$_2$MCP, 1Mc$_3$ECP, 224TMH	11DMCH, 1Mt$_2$ECP, 1Et$_3$-MCP, 1Et$_2$MCP, 1Mc$_3$-ECP, 224TMH	12.10	3.15
800	800	800	800	nO, O-2 (c), O-2 (t), 3MHp-2	nO		
804	807	811	—	1t$_2$DMCH, 1c$_2$c$_3$ TMCP	1t$_2$DMCH, 1c$_2$c$_3$TMCP		
807	811	814	—	1t$_3$DMCH, 1c$_4$DMCH, 244TMH	1t$_3$DMCH, 1c$_4$DMCH	12.24	3.18
822	823	824	826	223TMH, 22DM3EP, 3M 1:7 O(diene), 24 DMHp-1	223TMH, 22 DM3EP	1.34	0.37
829	829	830	832	44DMHp, 26DMHp, 4M 1:70 (diene), 24DMHp-1	44DMHp, 26DMHp	0.35	0.09
834	838	841	845	ECH, 33DMHp,	33DMHp	0.60	0.16
840	844	846	—	113TMCH, 233TMH, 2M3EH	233TMH, 2M3EH	0.30	0.08
—	—	853	854	234TMH, 6MO-1	234TMH	0.21	0.05
—	—	859	860	34DMHp, 4EHp, 2M1:7O (diene)	34DMHp, 4EHp	0.21	0.05
—	—	865	866	2MO, 4MO	2MO, 4MO	0.15	0.04
—	—	—	887	33DEP, N-1	33DEP	0.30	0.08
—	—	—	900	nN	nN	0.15	0.04

olefinic, naphthenic or aromatic hydrocarbons would have definitely given $I>900$ in TCEPE (Fig. 7). Regarding the peaks of $I<700$ in squalene (Table 6), these are definitely not paraffins, otherwise, the same index band would also have been present in the TCEPE chromatogram (Fig. 7). The peak index of 683 in TCEPE has been confirmed to be methylcyclopentane by injecting it as a pure reference.

(c) In F_4, peaks having I-values between 955 and 1000 in TCEPE (Fig. 8) represent naphthenes and olefins only, because the highest index obtained in the squalane column was 938 (Table 7). Mention may be made that the analysis of naphtha available in literature did not report the presence of olefinic hydrocarbons having more than seven carbon atoms. Thus, the chemical type of hydrocarbons in the index band of F_4 from 955 to 1000 in TCEPE may be taken to be naphthenic. This could be positively confirmed if retention indices of the corresponding napthenes were available in TCEPE. The peaks of I values from 800 to 817 in squalane at 86°C demonstrate

TABLE 7—ANALYSIS OF FRACTION 4

Retention Indices at Different Temperatures (°C), Sq.			Tentative Identification	Refined Identification	Area % in	
67	75	86			Fraction	Whole naphtha
1	2	3	4	5	6	7
793	796	800	11DMCH, 1Mt$_2$ECP, 1Et$_3$MCP 1Et$_2$MCP, 1Mc$_3$ECP, 224TMH	11DMCH, 1Mt$_2$ECP, 1Et$_3$ MCP, 1Et$_2$MCP, 1Mc$_3$ECP	—	—
800	800	800	nO, 0-2 (c), 0-2 (t), 3MHp-2	0-2 (c), 0-2 (t), 3MHp-2	1.67	0.67
807	812	815	1t$_2$DMCH, 1c$_2$c$_3$ TMCP	1t$_2$DMCH, 1c$_2$c$_3$TMCP	—	—
811	814	817	1t$_3$DMCH, 1c$_4$DMCH	1t$_3$DMCH, 1c$_4$DMCH	1.95	0.08
824	826	827	223TMH, 3M1:70 (diene), 22DM3EP 4M2Pr P-1	223TMH, 22DM3EP 4M2Pr P-1	—	—
831	832	833	44DMHp, 26DMHp, 4M1:70 (diene) 24DMHp-1	44DMHp, 26DMHp 24DMHp-1	—	—
834	838	842	nPrCP	nPrCP	—	—
839	842	846	ECH, 33DMHp	ECH, 33DMHp	—	—
845	849	853	113TMCH, 233TMH, 2M3EH	113TMCH	—	—
854	854	855	234TMH, 6MO-1	234TMH, 6MO-1	55.80	2.23
865	864	865	2MO, 4MO	2MO, 4MO	—	—
—	870	871	3MO	3MO	27.90	1.12
874	876	878	2245TMH, 23DM3EP	2245TMH, 23DM3EP	0.44	0.02
882	884	886	33DEP, Nonene-1	33DEP, Nonene-1	0.44	0.02
884	888	892	112TMCH, 55DM3EH	112TMCH, 55DM3EH	1.41	0.04
900	900	900	nN	nN	5.88	0.22
910	915	920	Cycloparaffins, cyclo-olefins Cyclodiolefins, bicyclo	Unidentified cycloparaffins	1.95	0.88
918	921	923	2345TMH	2345TMH	0.44	0.02
922	927	931	iso. Pr. CH	iso. Pr. CH	0.70	0.03
929	934	938	n Pr. CH, 2233TMH	n Pr. CH, 2233TMH	2.10	0.08

TABLE 8—ANALYSIS OF FRACTION 5

Retention Indices at Different Temperature (°C), Sq.			Tentative Identification	Positive Identification	Area % in	
67	75	86			Fraction	Whole naphtha
670	673	678	B$_z$	B$_z$	9.50	0.63
733	737	740	Naphthenes, Cyclo-olefins, Cyclo diolefins, Bicyclo	Cyclodiolefins	2.00	0.13
775	778	782	Tol	Tol	77.00	5.00
872	873	872	2 MO-1, 3MO	2 MO-1	0.76	0.05
906	910	915	224TM3EP, cyclo diolefins Napthenes, cyclo-olefins, Bicyclo	Bicyclo, Cyclo-olefins	0.75	0.05
925	926	927	4 iso Pr. Hp, Mono/di olefins	Mono olefins	4.00	0.26
930	930	932	27 DMO, Mono/diolefins	Mono olefins	2.21	0.14
934	936	938	234 TMHp, 334 TMHp, Cyclo-olefins, naphthenes	Naphthenes, cyclo-olefins	4.00	0.26

TABLE 9—ANALYSIS OF FRACTION 6

Synthetic Mixture			Retention Indices at Different Temperatures (°C), Sq.			Positive Identification	Area % in	
Component	86 I$_{Sq}$	98 I$_{TCEPE}$	67	75	86		Fraction	Whole naphtha
Tol	782	1180	773	777	782	Tol	1.79	0.18
EB$_Z$	872	1253	866	869	872	EB$_Z$	14.94	1.49
m, p-Xy	890	1270	884	887	890	m, p-Xy	81.67	8.17
o-Xy	908	1321	900	904	908	o-Xy	0.40	0.04
isoPrBz	926	1285	920	923	926	isoPrBz	1.20	0.12

TABLE 10—ANALYSIS OF FRACTION 7

Retention	Index in Sq. at °C		98 I$_{TCEPE}$	Positive Identification	Area % in	
67	75	86			Fraction	Whole naphtha
865	868	872	1253	EB$_Z$	0.65	0.02
884	887	890	1270	m p-Xy	12.52	0.44
900	904	908	1221	o-Xy	52.75	1.85
920	923	926	1285	isoPrB$_Z$	2.00	0.07
950	954	957	1338	n PrB$_Z$	8.07	0.28
965	968	971	1355	m, p, E. Tol	16,64	0.58
980	983	987	1381	oE. Tol.	—	—
983	985	987	1354	135TMB$_Z$	4.28	0.15
1000	1003	1006	1400	124TMB$_Z$	3.13	0.11

the absence of paraffins on the same basis as was discussed under (b).

(d) The fact that the index spectrum of the chromatogram of F$_5$ spans from 960 to 1180 in TCEPE and from 670 to 934 in squalane at 67° (Table 8) proves the absence of paraffins. The peaks of retention index values of 670 and 775 in squalane phase are indicated to be benzene and toluene respectively, after considering I and dI/dT values and have been confirmed from their index values of 1092 and 1180 at 98° in TCEPE (Fig. 9), obtained by separate injections of pure references. Most of the peaks in Table 8 could only be assigned structural types, individual identification not being possible due to the lack of data in both the liquid phases.

(e) The retention index spectra of F$_6$ spread from 782 to 926 in squalane and from 1180 to 1321 in TCEPE, the corresponding ranges of F$_7$ being 872 to 1006 and 1253 to 1400 (Figs. 10 & 11 and Tables 9 & 10). Obviously, paraffins are absent in both the fractions. The presence of other chemical types would involve $\triangle$I shifts of more than 247 index units. These large shifts are not possible with mono- and di-olefins, cycloparaffins and mono cycloolefins (Table 1). Acetylenes, triolefins, and cyclodiolefins may have a shift of this order, but their presence was not considered in this study because of non-availability of reported data. Most probably, only aromatic hydrocarbons are present in F$_6$ and F$_7$ (Tables 9 and 10), because (i) the number of peaks of each fraction is the same in both the squalane and the TCEPE chromatograms, (ii) I and dI/dT values of all the peaks of F$_6$ and F$_7$ in squalane tally exactly with the experimental values, and (iii) the experimental I-values of all the peaks of F$_6$ agree well with those of the aromatic hydrocarbons of Table 9. In the order of elution of the aromatic hydrocarbons reported in Tables 9 and 10 peak inversions may be noted in TCEPE as compared with squalane. The peak inversion in a polar liquid is predominantly confined to the ortho-substituted aromatic hydrocarbons. A comparison of these peak inversions with those of Stuckey[7] also corroborated the peak identification of F$_6$ and F$_7$.

The above special features have resulted from consideration of $\triangle$I values only of chemical types. Obviously, further valuable information will result from other parameters, like dI/dT and index-structure correlations of individual members, when these are available in TCEPE.

Basis of Peak Identification: The idea of using a pair of stationary liquids with opposite retention properties has been found to be very effective in the unambiguous characterization of peaks. The chromatograms presented in this paper were interpreted qualitatively giving the maximum stress on the retention index and parameters derived therefrom. Some of the important considerations upon which peak identification was based are summarized below:

(i) The preparative GC cuts were re-chromatographed from an analytical column, containing the same stationary liquid, in order to know the retention index distribution.

(ii) The retention index spectra of each preparative GC fraction from a non-polar and a polar column were compared for finding the presence or absence of various chemical types of hydrocarbons.

(iii) The area per cent, measured from the counts of a disc integrator trace, of a peak in squalane and its suspected counterpart in TCEPE was compared in order to be sure whether a peak in squalane contains one or more chemical types. When the two peaks have the same area per cent and close retention index in the two columns, only paraffins are probable. A composite peak in squalane, containing more than one chemical types, undergoes reduction in peak area in the TCEPE chromatogram, where different structural types are resolved completely.

(iv) Information on co-elution, peak inversion and various structural correlations of the hydrocarbons were also given due importance.

(v) A tentative identification table for each fraction was first made from considerations of retention behaviour, including I and dI/dT values in squalane. This table was then subjected to a rigorous scanning by the second set of identification parameters, viz. $\triangle$I, I and dI/dT values in the polar stationary liquid.

(vi) In some cases of uncertain identifications, reference compounds which were suspected to represent a peak, were used for the final matching of coelution, peak shifting behaviour, I, $\triangle$ I and dI/dT values.

Refinement of the Scheme and its Suggested Applications: Even for the analysis of naphtha, the full potentialities of the scheme proposed here could not be utilized, because (i) the essential data of I and dI/dT in TCEPE are not available at present for all the hydrocarbons whose corresponding values are known in squalane and (ii) the significance of the intercepts of the universal I-T straight lines *vis-a-vis* the solute structure, could not be seen at the present, although it is believed to be an important and sensitive identification parameter.

The stock of I-values of the hydrocarbons in TCEPE can, however, be increased by the experimental data of a few representative compounds, followed by graphical correlations with squalane data by the methods of Mitra and Saha[24] and Walraven *et al.*[22]

The distribution of olefins in naphtha can be thoroughly studied by a double preparative GC fractionation procedure. Each fraction from squalane is subdivided into chemical types in TCEPE. The olefin subfractions can then be conveniently and completely resolved in suitable high efficiency columns. The existing information from literature on the qualitative and quantitative analysis of the olefins in naphthas is inadequate and conflicting. This principle can be generalized for the analyses of a class of compounds present in traces in a complex sample.

Although naphtha has been shown as an illustration, it should be clearly understood that hydrocarbons of higher boiling ranges can also be analysed efficiently by this scheme. Moreover, this scheme may be easily extended to complex samples belonging to homologous series other than the hydrocarbons, provided, of course, the choice of the pair of stationary liquids is proper and the desired retention data of the components are available in them.

Quantitative Results: The customary procedures for the quantitative analysis of naphtha were not rigorously followed in this work neither in the preparation of the representative sample, nor in the quantitative aspect of fraction collection in the preparative GC. An overall loss of about 25 per cent was observed in the preparative fractions of naphtha. By injecting known amounts of n-hexane and n-octane separately, collection efficiency was found to be 70 and 95 per cent respectively. Therefore, the total sample loss in the preparative GC was apportioned to F_1 and F_2 and the quantitative estimation of the other higher fractions are given in the last two columns of the identification tables (Tables 6 to 10).

Acknowledgements

The authors' thanks are due to Dr. A. Sinha for his interest in this work. Thanks are also due to Mr. L. S. Ettre, Prof. A. I. M. Keulemans, Prof. A. Zlatkis and Dr. D. A. Tourres for their constructive comments.

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[Original mss. received on Sept. 23, 1972]

UDC 541.128+621.496:542.96:546.26

The effect of temperature on the thermal conductivity (λ_s) of some porous catalysts used for carbochemical synthesis has been studied. Utilizing λ_s of the high temperature shift reaction catalyst, the temperature gradient within the pellet has been evaluated using the Prater's equation. It has been observed that the λ_s of the catalysts increases with rise of temperature, its influence on the temperature gradient of shift reaction catalyst is non-significant. It may, therefore, be concluded that λ_s at a temperature lower than the optimum reaction temperature can be used for the evaluation of temperature gradient of this catalyst for practical design purposes.

Heat Transfer in the Catalyst Used for Carbo-Chemical Synthesis

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There has been considerable interest recently in problems related to mass and heat diffusion in porous catalyst particles. Assuming the entire catalyst particle to be isothermal, the analysis of diffusion effects has been frequently applied in experimental work. But when the chemical reaction is accompanied by a heat effect, appreciable temperature gradient, along with mass concentration gradient may exist within the particle, because the reaction components and heat of reaction must be transferred into or out of the catalyst particle by simultaneous mass and heat transfer processes. In the cases of pronounced exothermic or endothermic reactions as indicated theoretically by Wheeler[1,2] and Prater[3], the temperature difference between the particle centre and the surface of the particle may be of the order of 100°C. Damkohler[12] has derived an equation for estimating such temperature differences. Since then a number of workers have investigated the effect of intra particle temperatures gradient upon the kinetics of heterogeneous catalytic processes[4–11,18,24]. Furthermore, the small changes in temperature may result in very significant changes in the process rate and in the apparent activation energy. It is suggested that 'hot spots'[25] in catalytic reactors and sintering of catalysts[27] can be caused by such effects, thus causing damage to the catalyst itself. The existence of this temperature gradient has recently been varified experimentally by a number of workers[15,19–23].

The temperature gradient across the profile of catalyst layer would be dependent on the geometrical shape of the catalyst pellet. But Prater has derived one relation which involves diffusion of the reactants and their concentrations at the surface and inside the bulk as well as heat of reaction. This relation is independent of the geometrical shape of the pellet but would be very much dependent on its thermal conductivity. Although the magnitude of the nonisothermal effects is very strongly dependent on the thermal conductivity of particles, very little information is available on the thermal conductivity of porous catalysts. The problem of thermal conductivities of packed beds has been studied extensively[16], but information on the experimental determination of catalytic thermal conductivity has been given only by a few workers[13,14,17]. They have measured only a few industrial catalyst samples, but the measurement with respect to their variable temperature has not been attempted. A knowledge of such variation would be useful particularly for determining the actual temperature gradient in the catalyst pellet, as the bulk property of the sample at operating condition differs very much from that of the sample at room temperature. Roy *et al*[28] have developed an apparatus based on heat flow comparator method which has been successfully utilized to determine thermal conductivity of small catalyst pellet at different mean temperatures.

The present investigation was taken up to measure thermal conductivity of some porous catalyst pellets used in carbo-chemical synthesis and to throw some light on the variation of thermal conductivity with variable temperature. Further, the thermal conductivity value has been utilized to compute the thermal gradient across the bulk of the catalyst pellet to find its importance, taking shift reaction catalyst as an example.

Experimental

The following different catalyst samples have been taken for this investigation: (1) shift reaction for (a) high and (b) low temperature, (2) reformation and (3) desulphurization catalysts. Catalyst samples used were commercially available in the different geometrical forms and sizes, and it was not possible to use them as such. So, these samples were powdered to −85 mesh BSS and the final pellets in the form of 10 mm. diam. cylinders were compressed from the powder, utilizing Carver Model B laboratory press. Pressing procedure employed was such to produce reproducible pellets with internally consistent properties, with maximum variation of density, viz. about ±1.8 per cent, irrespective of density level. The density homogeneity of the pellets was verified by measuring the density of individual sections of the pellets.

Measurement of Thermal Conductivity: Thermal conductivity of these pellets was measured by the apparatus described by Roy *et al*[28]. In this method sample pellet was pressed in between two metallic bars of known thermal conductivity and when a steady state was reached, temperatures t_1, t_2, t_3 and t_4 were measured. Thermal conductivity was calculated utilizing the following expression.

$$\lambda_s = \lambda \frac{d_s}{2d}\left[\frac{t_1-t_4}{t_2-t_3}-1\right]$$

where, λ_s = Thermal conductivity of the specimen pellet.
d_s = Length of the specimen pellet.
λ = Thermal conductivity of metallic bars.
d = Distance between two thermocouples fitted on any of the metallic bars.
t_1, t_2, t_3, & t_4—Temperature of thermocouples T_1, T_2, T_3 and T_4 fitted on metallic bars[28].

Thermal conductivity of these catalyst pellets was measured at different mean temperatures ranging from 50 to 150°C. These measurements were carried out utilizing two numbers of catalyst pellets in each case to ascertain the accuracy of the measurements.

Computation of Temperature Gradient in the Catalyst Pellet: The equation as developed by Prater[3] has been utilized for this purpose, which is as follows:

$$(T-T_s)=\frac{-\triangle H\ De}{K}(C_s-C)$$

where, T is the temperature (°C) at all points within the particle which have a concentration of reactant C (mole/cm^3) and T_s is the temperature (°C) at the surface of the particle.

C_s is the concentration of the reactant at the surface of the particle, mole/cm^3

TABLE 1—THERMAL CONDUCTIVITY OF CATALYST SAMPLES AT DIFFERENT TEMPERATURES

Sl. No.	Catalyst Designation	Type	Density, g./cc.	$\lambda_s \times 10^3$ g., cal. sec^{-1}, cm.$^{-2}$, °C^{-1} cm. at		
				50°C	100°C	150°C
1.	High Temp. shift reaction	Iron-oxide/Cr-oxide	2.524	2.95	3.96	4.20
2.	Low Temp. shift reaction	Cu-oxide/Zn-oxide	4.35	1.30	1.55	1.79
3.	Reformation	Ni/Al_2O_3	2.04	3.78	4.51	5.23
4.	Desulphurization	Iron-oxide	2.22	2.43	2.94	4.56

TABLE 2—VARIATION IN TEMPERATURE GRADIENT WITH THERMAL CONDUCTIVITY OF HIGH TEMPERATURE CO-CONVERSION CATALYST

Sl. No.	Temperature (λ_s being measured at), °C	λ_s, g cal sec^{-1} cm.$^{-2}$, °C^{-1} cm.	De at[26] 360°C and 25 Atmos., cm^2./hr.	$-\triangle H$[26] at 460°C cal g. mol.	C_s-C, mol./cc	$T-T_s$, °C
1.	50	2.95×10^{-3}	123	8970	0.37×10^{-4}	3.8
2.	150	4.2×10^{-3}	,,	,,	,,	2.7

$\triangle H$ is the heat of reaction, cal/mole (negative values mean exothermic reaction).

D_e is the effective diffusivity of the particle, cm²/sec.

K is the thermal conductivity of the particle, cal/sec. cm.,°C

The temperature gradient has been calculated at the operating temperature of 360°C and utilizing thermal conductivity values determined at 50°C, and 150°C, De and $\triangle H$ from literature[26] and C & C_s from feed data of industrial reactor.

Results and Discussion

The experimental results are summarized in Tables 1 and 2. The variation of λ_s with temperature is shown in Fig. 1. The thermal conductivity (λ_s) data of different industrial catalysts (Table 1, Fig. 1) reveal that λ_s of these catalyst pellets increases with rise in temperature. But of the four type of catalysts studied, value of desulphurization and reformation catalyst increases more significantly with rise of temperature than in the case of other two. The temperature gradient ($T-T_s$) as calculated in the case of high temperature shift reaction, utilizing the thermal conductivity value at 50°C is 3.8°C and that utilizing at 150°C is 2.7°C (Table 2). These temperature gradients are not large and their variation is also non-significant with rise in temperature. These results clearly indicate that such computation utilizing value at near ambient temperature may be utilized for all practical purposes in this case. It may however lead to erroneous conclusion if the λ_s of a catalyst varies significantly with rise of temperature, resulting in large temperature gradient.

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Superintendent, Physical Research Wing, for his interest in this work.

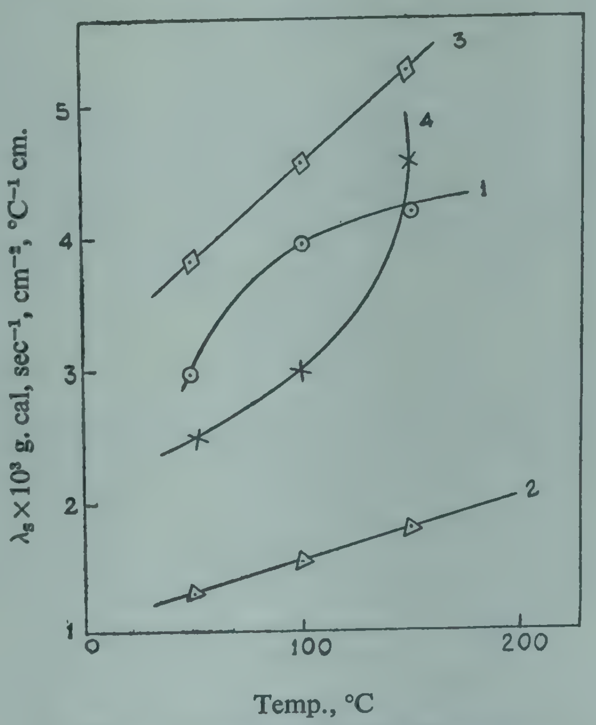

Fig. 1—Variation of λs with Temperature

1. H.T. Shift Reaction
2. L.T. Shift Reaction
3. Reformation
4. Desulphurization

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[Original mss. received on Aug. 28, 1972]

UDC 543.6:549.222:544.66:546.18-3

A direct estimation of phosphorus in rock phosphate by using wide-line NMR spectrometer has been described. The advantages and limitations of this method over the commonly used techniques have been stated. The results presented here are found to be in good agreement with those by the chemical analysis. Moreover, this method is nondestructive and the sample can be recovered completely after the analysis.

Assay of Phosphorus in Rock Phosphate by Wide-Line NMR

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The application of nuclear magnetic resonance (NMR) spectrometry as a tool in chemical analysis was first introduced by Shoolery[1] in 1954. Since then, the analysis of phosphates by NMR had mainly been carried out by the high resolution techniques[2–4] to distinguish between the different types and to estimate them separately. The NMR techniques can also be employed to analyse the phosphorus content of rock phosphates, minerals, industrial products, etc. However, for fertilizer applications, it is the total assay of phosphorus which is more important. For such purposes, the wide-line technique, in preference to the high resolution NMR, should be utilized. The reasons for such preference are: (i) high resolution NMR necessarily involves observations in the liquid phase, whereas wide-line NMR can utilize the solid rock samples directly, (ii) the rocks are naturally doped with paramagnetic ions, like iron, copper, etc., which are present in sufficiently large amounts to reduce the spin-lattice relaxation time sufficiently to permit rapid spectral runs, whereas high resolution NMR requires a comparatively longer scanning time.

It is worthwhile mentioning here that for the determination of phosphorus both chemical and spectrochemical methods have been used with varying degree of success. For the lower concentration below 0.50 per cent phosphorus pentoxide, vanadium phosphomolybdate[5] and polarographic[6] methods are being used, while for higher concentration the magnesium pyrophosphate method[7] is recommended. Spectral methods, like x-ray fluorescence,[8] atomic absorption spectrophotometry[9] and flame emission[10], are also used for the determination of phosphorus, but none of them is free from spectral interference effects.

The nuclear resonance methods have two notable advantages over the commonly used techniques, particularly chemical and spectrochemical methods, viz. freedom from interference and rapidity of analysis. The accuracy is quite comparable, as can be seen from the results. Moreover, it is a nondestructive method, so the sample can be recovered after the analysis. The only limitation in this method is that the lowest measurable concentration of phosphorus is about 0.8 per cent. However, where rock samples are assayed for their suitability in phosphatic fertilizer manufacture, such low limits will never come in the way of applicability of this technique.

Experimental

The experiment was carried out with a Bruker-Physik wide-line NMR spectrometer B—KR 10/30 at room temperature (27°C) using a 10 MHz constant frequency excitation. Rock samples from various places containing different amounts of phosphorus were taken in the powder form. To get the maximum sensitivity, powdered samples having the same dimensions as that of the r.f. coil were taken within a thin-walled sample tube of glass. This required about 2 to 2.5 g. of the rock sample. The spectrometer was calibrated against a standard rock sample containing a known amount of phosphorus which had been analysed by the National Bureau of Standard (N.B.S.) method giving 34.3 per cent of phosphorus pentoxide (P_2O_5). To improve the signal-to-noise ratio of the output NMR signal, a low-pass filter incorporating a large filter time-constant of about 7 sec. was used. The absorption mode signal was recorded employing 100 milligauss modulation at 175 Hz. Equal amounts of samples taken from the different varieties of rocks were weighed and the corresponding phosphorus absorption signals were recorded. These were compared with the signal of the same weight of the standard sample. Moreover, for each sample, the absorption signal was recorded several times to check the reliability of the instrument. From the reliable records, the mean area of the absorption signal of each rock sample was calculated and compared with that of the N.B.S. standard. This allowed direct determination of phosphorus pentoxide (P_2O_5) in the rock sample.

The experimental results are shown in the Table 1 which also contains the values of chemical analysis for comparison. The same results are illustrated in Fig. 1

TABLE 1—P_2O_5 IN ROCK PHOSPHATE

By Chemical Analysis, %	By NMR Method, %	Total Experimental Scatter, ± %	Percentage of Deviation from Chemical Analysis
41.90	41.25	0.84	−1.55
38.24	39.03	1.17	+2.06
37.00	37.08	0.75	+0.22
35.00	34.90	0.70	−0.28
32.80	32.54	0.94	−0.74
30.00	30.18	0.60	+0.60
25.00	25.58	0.50	+2.32
19.00	19.12	0.38	+0.63
15.00	14.70	0.45	−2.00
10.00	10.01	0.15	+0.10
5.00	4.97	0.25	−0.60
2.50	2.80	0.35	+12.00

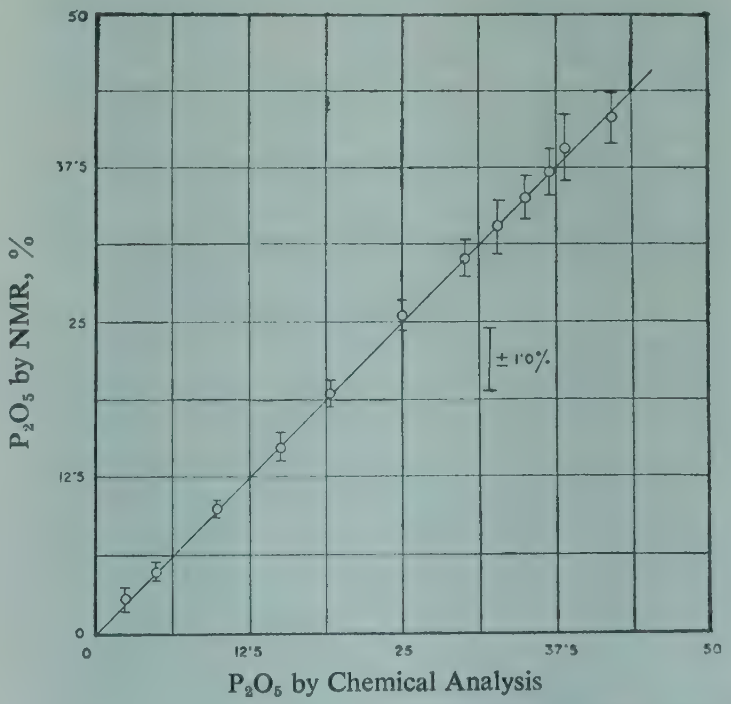

Fig 1—P_2O_5 concentration as determined by NMR plotted against chemically computed values. The far length denotes experimental scattering.

for observing the validity of this method. The Fig. 1 clearly indicates that the NMR results are in good agreement with those of the chemical analysis. It is to be noted that the time of estimation for each sample is only few minutes and free from any interference.

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[Original mss. received on Dec. 7, 1972]

UDC 620.193:666.76:662-613

Corrosion of the acidic and basic type refractories by coal ash slag has been studied. It has been observed that the fire-brick is badly corroded even at 1450°C, while at 1600°C the slag penetrates the bulk where it interacts with the refractory forming well-developed mullite crystals. In the cases of chromite, magnesite and magnesite chrome bricks, the slag also penetrates the body but the interaction is not so predominant and does not deform as that in fire-brick refractory.

Corrosion of Refractories by Coal Ash

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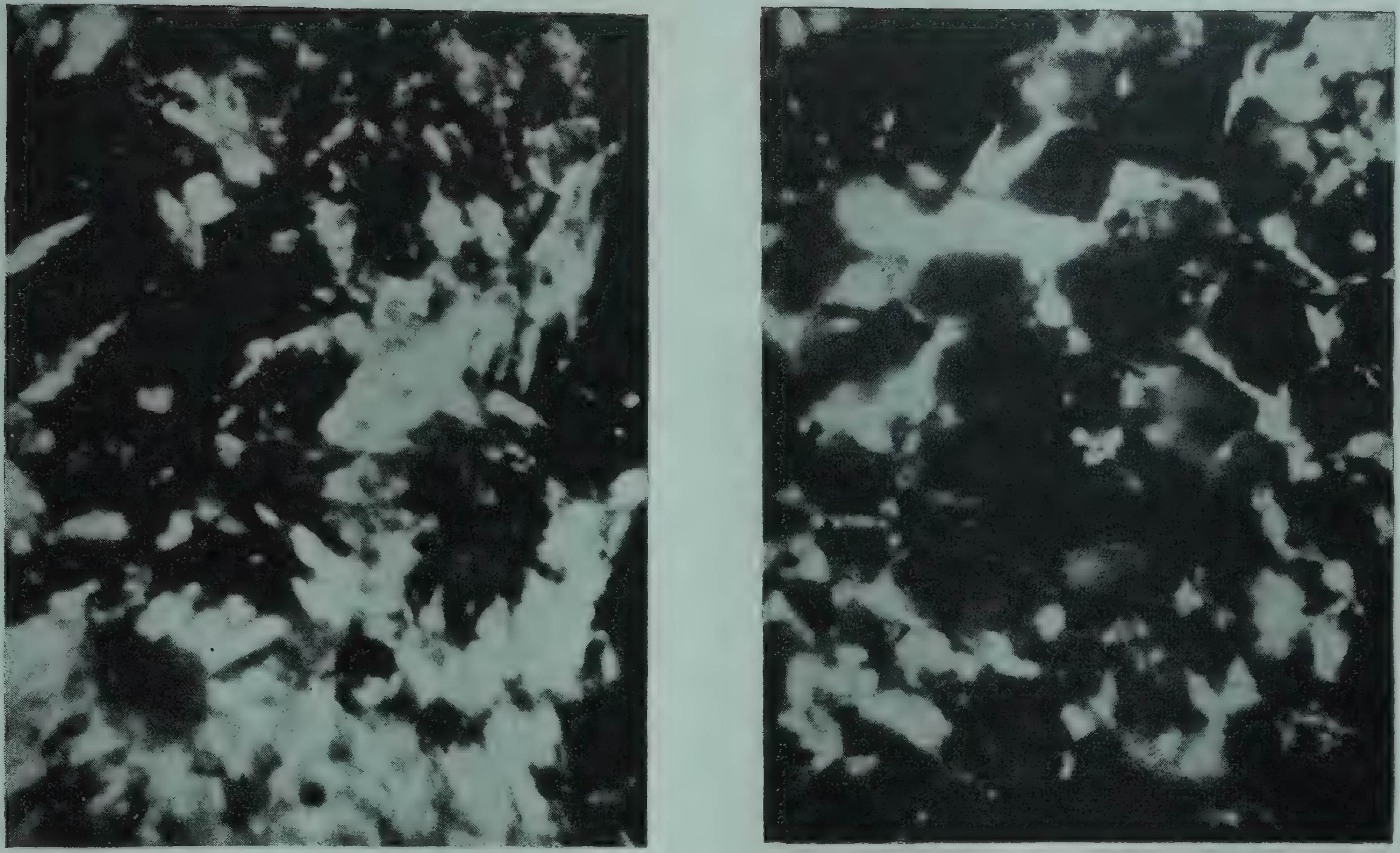
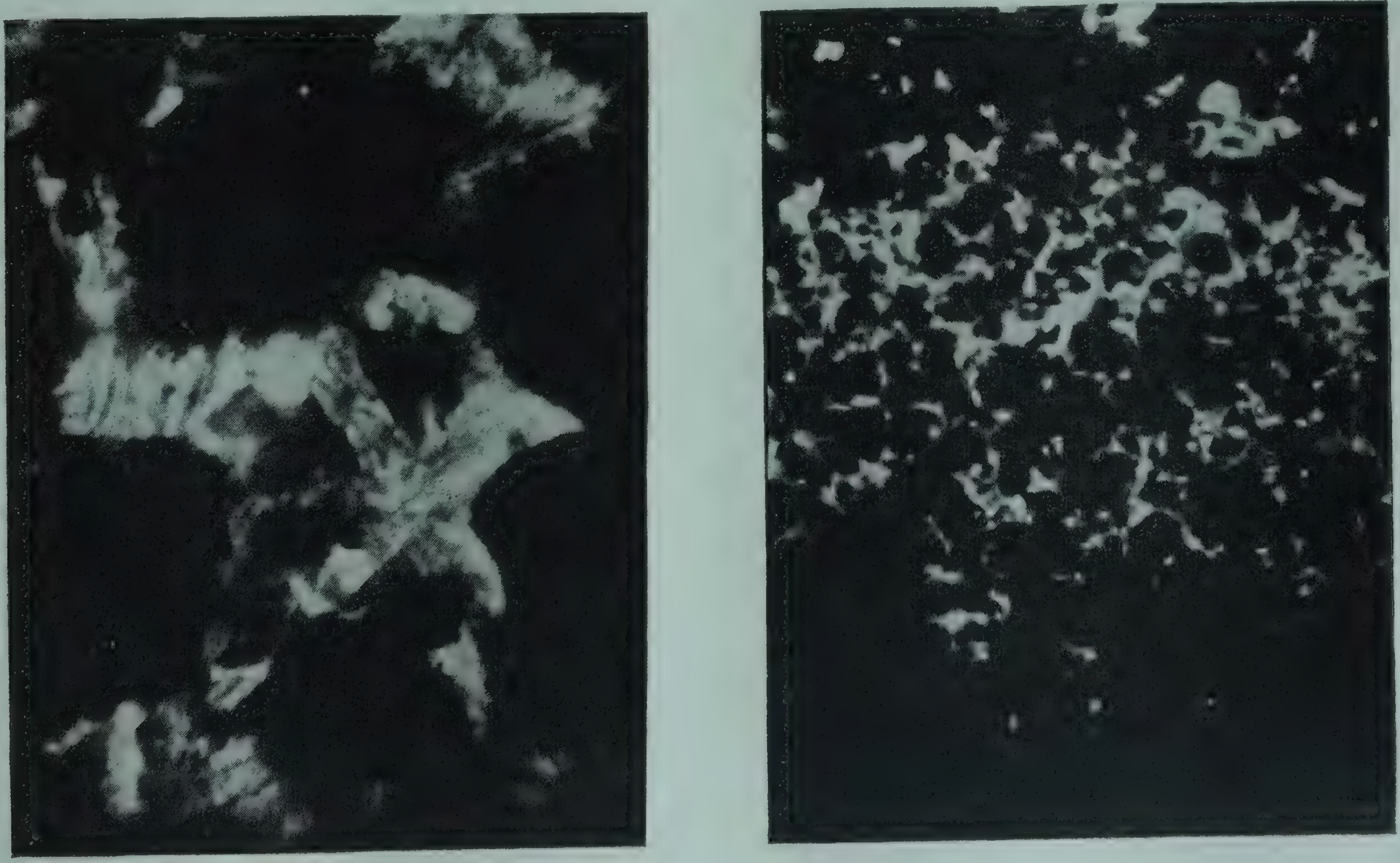
Coal ash is known to corrode acid refractories at elevated temperatures. Corrosion of sillimanite refractory by coal ash slag has been studied by a number of workers[1–3]. Corrosion of alumina refractories by iron-and magnesium-rich slag of Victorian brown coal was studied, and it has been established that corrosion is caused mainly on the surface. The iron and magnesium oxides, together with an alkali form a low m.p. glass at the slag brick interface. This glass contains spinel and cordierite with concomitant recrystallization of mullite. In fact, mullite content has been used to predict slag resistance of alumino-silicate refractories, used mostly in power stations.[4]

Acid refractories, such as fire-bricks, are commonly used in the boiler plants. The average life of these refractories depend upon their grade as well as the nature of the coal ash. In chemical plants, coal having 25-30 per cent ash is used for boiler plant where the life of such refractory lining varies from 3 to 6 months. Unless the lining is changed, the corroded refractory impairs badly the thermal efficiency of the boiler resulting in production loss to a significant amount. Most of the investigations are related to corrosion of acidic refractories by coal ash slags, but the behaviour of such slags with non-acidic refractories has not been established.



A—Well developed mullite grains within an opaque glassy mass of fire brick refractory.

C—Disintegrated chromia grains with periclase surrounded by forsterite of magnesite chrome refractory.



B—Forsterite grains with agglomerated chromia of chromite refractory.

D—Periclase grains of bigger size due to composition of smaller grains of magnesite refractory.

Fig. 1—Microphotographs of the Thin Sections of Corroded Samples of Refractories (× 100 with cross nicol)

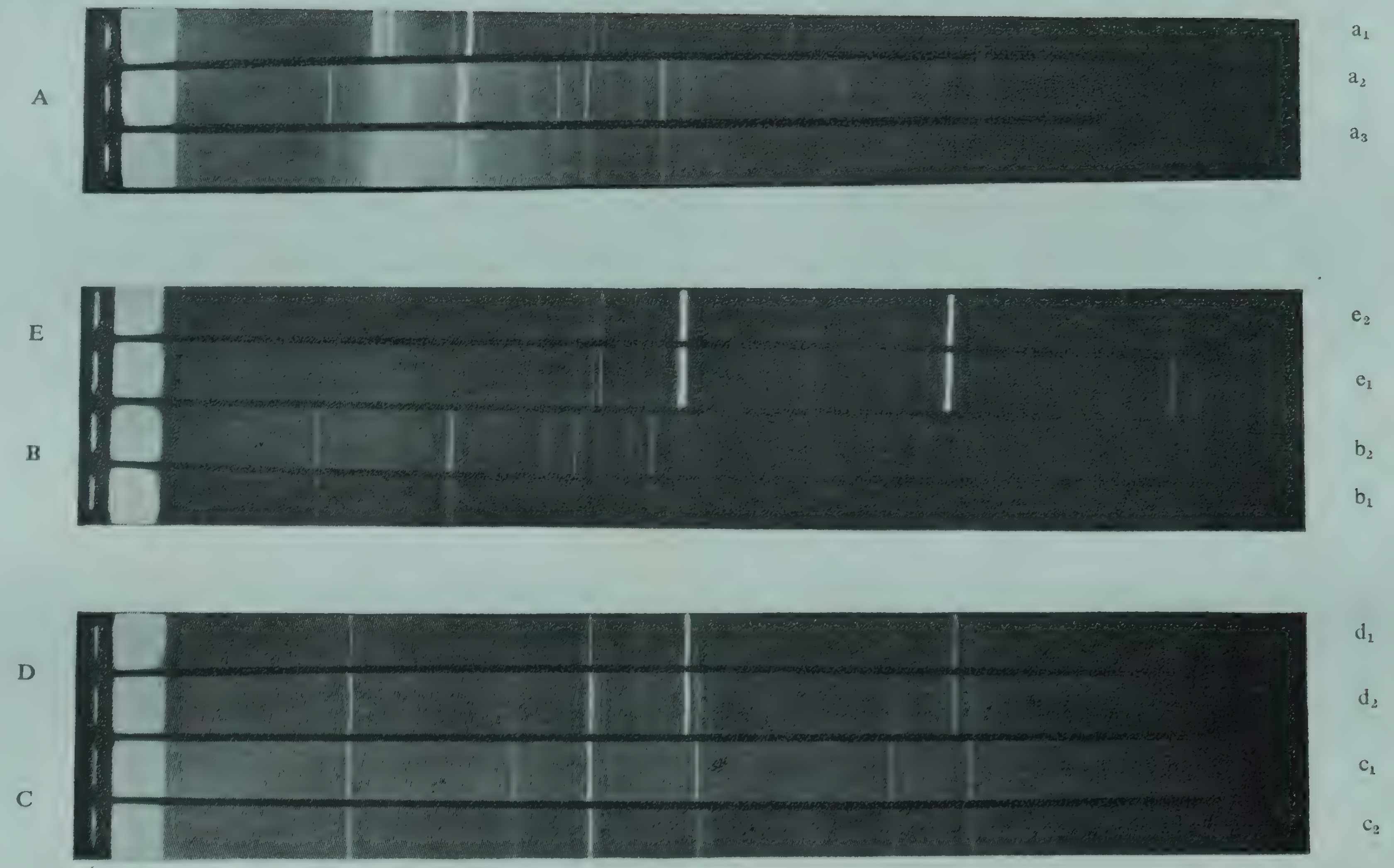


Fig. 2—X-ray Diffraction Patterns of Coal Ash and Corroded Samples.

A—Coal ash (a_1), coal ash heated to 1450°C (a_2) and coal ash heated to 1600°C (a_3)
B—Interface of the corroded fire brick heated to 1450°C (b_1) and heated to 1600°C (b_2)
C—Interface of the corroded chromite brick heated to 1450°C (c_1) and heated to 1600°C (c_2)
D—Interface of the corroded magnesite chrome brick heated to 1450°C (d_1) and heated to 1600°C (d_2)
E—Interface of the corroded magnesite chrome brick heated to 1450°C (e_1) and heated to 1600°C (e_2)

It is with this view that the corrosion of both acid and basic type refractories by slag formed from high ash containing coal was taken up in the present investigation.

Experimental

For this investigation, coal having 27 per cent ash was selected and refractories studied were fire-brick, magnesite, chromite and magnesite chrome bricks. The coal ash was prepared by burning powdered coal in the oxidizing atmosphere and the resulting ash was used. The fusion temperature of this coal ash was found to be 1420-1430°C which was quite below those of the refractories.

Small rectangular blocks of size 3″×2″×1″ were cut out of the refractory bricks by a diamond wheel rock cutter. A small cavity was made in each of these rectangular blocks so as to accommodate 5 g. of coal ash. The physical characteristics and chemical composition of these refractories are shown in Table 1.

TABLE 1—PHYSICAL CHARACTERISTICS AND CHEMICAL COMPOSITION OF REFRACTORIES

Sl. No.	Refractory Sample	Chemical Composition, %	Fusion Temperature, °C	Porosity, %
1.	Fire-brick	Al_2O_3 — 42.44 SiO_2 — 55.60	1720	25
2.	Magnesite	Fe_2O_3 — 5.0 SiO_2 — 5.6 MgO — 88.0 Cr_2O_3 — Nil	>1860	20
3.	Magnesite chrome	Fe_2O_3 — 6.7 SiO_2 — 5.6 MgO — 64.66 Cr_2O_3 — 18.0	>1860	24
4.	Chromite	Fe_2O_3 — 13.5 SiO_2 — Nil MgO — 24.5 Cr_2O_3 — 44.0	>1790	23

Corrosion Study of Refractory Blocks with Coal Ash: 5 g. of coal ash was taken in each of the refractory blocks and heated in a carbon-resistance furnace at two different temperatures, viz. 1450 and 1600°C, for 1 hr. The furnace atmosphere was found to be slightly reducing due to the presence of carbon monoxide. When the heating was over, the blocks were cooled inside the furnace. The time required to heat and cool to the ambient temperature was 7 to 8 hr. in each case. The ash was also heated to the same temperatures separately in platinum crucible.

Microscopic Studies: The corroded surface of all refractory blocks were examined under polarizing microscope after making their thin sections. Microphotographs are shown in Fig. 1.

X-ray Analysis: X-ray diffraction patterns of coal ash, before and after heat treatment, and the scrap (upto depth of 2-3 mm.) from the interface of the corroded refractory blocks were taken by a Guinear focussing camera. Cuk$_\alpha$ radiation generated at 40 KV, 20 mA in a Philips 1011 unit was utilized and the time of exposure was 6 hr. X-ray photographs are shown in Fig. 2.

The phases identified by x-ray and microscopic studies in the corroded surface are shown in Table 2.

Results and Discussion

X-ray examination of the coal ash sample (Fig. 2A) reveals that quartz is the major constituent. Other constituents detected are gehlenite (C_2AS) and mullite, which are present in small quantities. On heating the ash more mullite crystals develop and form the major phase at 1600°C.

The textures of refractory bricks as observed under microscope have already been reported.[6] A critical examination of the corroded surface of the refractories reveals that different refractories have been attacked by coal ash slag in different manner. The penetration of slag inside the bulk of the refractory is also not the same although their porosity is of the same order (20-25 per cent, Table 1). In each case, however, the degree of corrosion increases with temperature. At 1600°C, the refractory

TABLE 2—PHASES IDENTIFIED IN CORRODED SURFACE OF THE REFRACTORIES

Nature of Study	Fire-brick	Chromite Brick	Magnesite Chrome Brick	Magnesite Brick
Microscopic	Mullite & Glass	Chromia and Forsterite	Chromia, periclase and forsterite with a small amount of spinel	Periclase
X-ray	Mullite	Chromia and Forsterite	Chromia, periclase, forsterite and traces of spinel	Periclase

structure of fire-bricks collapses completely. The microscopic examination reveals (Fig. 1A) that the quartz grains at the interface of the refractory disappear when heated to 1450°C and mullite crystals within an opaque glassy melt are formed as a result of interaction of silica with slag. Unlike those present inside the bulk of the refractory block, these mullite grains are bigger in size and very well developed (Fig. 2B). Further, the corrosion is enhanced at higher temperature, more matrix material dissolves in the glassy melt causing structural collapse of the refractory.

There is no visible corrosion of chromite brick with the slag at 1450°C, whereas at 1600°C a portion of chromite refractory is dissolved out by slag and the rest penetrates the bulk of the refractory brick. Moreover, chromite brick contains a sizable quantity of magnesium oxide (Table 1) which evidently reacts with coal ash to form forsterite grains. This is quite clear from the microscopic examination revealing (Fig. 1B) that the opaque chromia grains are more or less agglomerated and there is some reaction of the slag with chromite brick resulting in the formation of a new crystalline phase, viz. forsterite (Table 2). This has been confirmed by x-ray study also (Fig. 2C).

The slag penetrates completely the body of magnesite chrome refractory at 1450°C as well as at higher temperature. The higher degree of penetration is caused due to the slow removal of periclase grains in the form of spinel, as a result of corrosion. Further, this penetration is also due to development of more pores in the intergranular zones as a result of disintegration of chromia grains forming matrix after disintegration (Fig. 1C).

The slag also penetrates the magnesite refractory at 1450°C and this penetration is enhanced at higher temperature but surface reaction is negligible. Only the periclase grains are more agglomorated and diffused (Fig. 1D). As a result of this change, the individual grains become polygonal and are more compacted. This enables development of more pores inside the bulk but the bridging among the particles is still retained by the parent matrix.

Thus, it is evident from the results that in spite of slag penetration in all the basic refractories they do not deform like fire-brick.

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Superintendent, Physical Research Wing, of this division for his encouragement.

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[Original mss. received on July 24, 1972]

UDC 621.3.013.8.025-087,001.4

The principle behind sampling of signal is explained in elementary terms. The conventional methods of progressive sampling are mentioned to illustrate the use of ramp voltages in such circuits. A new simple method of sampling periodic signals of predetermined frequencies is discussed, where progression is achieved without the use of ramps. Two close-lying frequencies are utilized, one to drive the system under investigation and the other to operate the sampling mechanism, so that the sample point is progressively shifted.

A Progressive Sampling Technique Suitable for Recording Systems Response under A.C. Excitation

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Displaying magnetic hysteresis loops or B-H loops, as they are termed in text books, is rather easy[1,2] if you are content to use an oscilloscope for observation. But try to record them on an X-Y recorder and all the fun is gone. Your recorder simply cannot respond to the fast signals, it is not built to take it. Slow down the cycle rate? Well, one must not forget what Faraday had said about rates of change of flux and induced voltages. A typical X-Y recorder has a response time of about five seconds for full scale travel. Allow ten times as much for the sake of fidelity, so we arrive at fifty seconds as the cycle time—it hardly remains an AC phenomenon at all and the signal is irretrievably lost in noise.

It was this problem which led us to design the sampling circuit that we are now talking about. True, there were methods available to build a recording B-H loop tracer, but these employed cumbersome galvanometer photocell systems[3], which we wanted to avoid. A sampling method was previously used by Grover[4], but it had certain drawbacks. In trying to get around these defects, a new system of sampling was evolved which could be of more general applicability than mere hysteresis loop tracing. Indeed, it can be used to record the AC response of any electrical system with ordinary recorders at some predetermined cycle rates, and yet it is far simpler than, say, the circuit used in some commercially available sampling oscilloscopes. But before starting forthright with the description of our system, we feel that it will be better if we say something about sampling in general.

Sampling

The frustrating problem of adapting slow electromechanical devices, like galvanometers, recorders, etc., to display fast repetitive signals must have faced research workers in various disciplines. That is precisely where the sampling circuits come in, and these can be elaborated a little so that everybody can have an insight into their functioning. In the subsequent discussion we shall refer to the villain of the piece, the slow moving device, as simply 'the device'.

We imagine now the signal wave form to be chopped up into a large number of very small bits. Let us also consider the posibility of installing a circuit that can select only one bit in one signal cycle and feed it to the device. During the next cycle, the adjacent bit is picked up, and so on. It is at once clear that the device will have to respond to only a small amount of change, from one bit to the next, during the period of one cycle. Of course, some arrangement has to be provided to hold the reading corresponding to one bit till the next bit arrives. Like this, the entire signal form will be scanned at a leisurely pace and the device will be spared from the pains of following the hectic changes through the whole gamut of signal intensity within the brief span of one single cycle.

The small bits of the signal, which are selected one at a time out of the complete signal form, are called samples and the process is called 'sampling'.

Construction

Let us now come down to the brass tacks. Broadly speaking, three different functional units are necessary in the process. These are: (i) a circuit to pick up the bits, i.e. the samples from the wave form, (ii) an arrangement to shift the sample point by one step in each cycle, and (iii) a memory device to hold the information during one cycle, which must be erased just before the next sample arrives. This simple description does not include amplifiers and impedance matching stages, which are to be used as required.

The first function is served by a circuit called 'gate'. The nomenclature is quite graphic. It blocks the passage of a signal till the gate is opened by a gate pulse. In this open condition, the signal can pass freely, but only as long as the gate pulse is present. The moment the gate pulse is removed the passage is blocked again. By using a gate pulse of very short duration, the gate is opened for just a little while and a very small portion of the signal can be admitted to the other side. By now it must have been obvious how the gate circuit can be used to pick up the samples. Various types of gate circuits are in use. Any standard text book on pulse circuitry may be referred to for the details. In our set-up biased diode gates were used.

Now comes the second and the most intriguing aspect of the problem, shifting the sample point in each cycle. In the cheaper sampling oscilloscopes, the sample points are chosen at random. But that is feasible only in the case of the almost inertialess electron beam of the cathode ray tube. In pen recorders, random sampling will result in violent erratic movements of the pen and no information will be available from the trace. In such cases 'progressive sampling' is employed, where the sample point is systematically advanced in one direction. In one versatile sampling oscilloscope an elaborate circuitry is used to achieve this. But such complexity is necessary in view of the diverse situations that can be tackled by the 'scope,—frequencies from D.C. to gigahertz region and signals which have to be repetitive but not necessarily periodic. Our task was much simpler, as we had designed only for periodic signals. Grover, who had also this advantage, solved the problem by operating a gate circuit set to trigger at a preset voltage level. A steadily increasing voltage (called a ramp voltage by electronic engineers) was superposed on the cyclic signal, so that in each successive cycle the sample point was shifted by an equal voltage step, as shown in Fig. 1. The sample is taken whenever the sum of the signal plus the ramp voltage just exceeds the preset trigger level. The trouble with this system is that the sample points tend to come far apart as the signal flattens out. Unfortunately, for many applications, the interest centres about the region of saturation, where the system's response becomes flat. For such cases, the ramp voltage has to be specially shaped to compensate for the varying slope of the signal. That was actually the practice followed by Grover, but it preassumes that the signal shape is known, which will not be true in majority of the cases studied. Another disadvantage is that in this method, one obtains only a part of the cycle, either the rising half or the falling half of the signal. This point may not be immediately apparent, but it follows from a characteristic of trigger circuits, that they can be designed to operate when the input either just exceeds or just falls short of the preset level, but not both ways. To obtain the full signal form the system has to be duplicated.

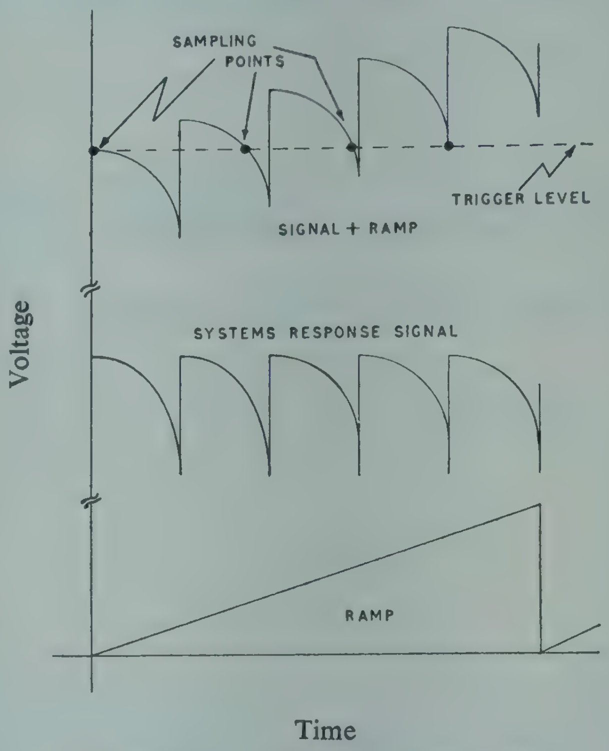

Fig. 1—Progression by Shifting of Trigger level in Grover's Method

Both these difficulties can be avoided if the sample points are taken at equal time intervals instead of equal voltage intervals. In fact, this is the mode used in all the better sampling circuits, The most common practice is to use a ramp voltage again, but in this case it is a repetitive ramp, beginning afresh with each new signal cycle. The sample is taken the moment the ramp voltage reaches the preset trigger level. At each cycle the trigger level is shifted by an equal step, so that the ramp voltage takes progressively longer time to reach the trigger level. We are going into all these details to put stress on the fact that the progression is achieved through the ramp voltage, which features in all the methods. Our present method, however, marks a departure from the set pattern.

Advancing the Sample Point

Our way to do it was to take two wave forms with slightly different frequencies, make the faster one to drive the system under investigation and let the other operate the sampling mechanism. At each cycle, the sample point will shift slightly, the phase advancing a little at each step. This will be clear from Fig. 2. Obviously, the closer the two frequencies, the closer will the sample points be and the quality of the recorder trace will correspondingly improve. The sampling patterns according to Grover's method and our method are compared in Fig. 3. The frequencies used by us were 25 and 25.0025 Hz. Now, anyone who has worked with low-frequency oscillators will at once protest that it is impossible to maintain two oscillators at such a minute frequency difference apart, and we shall agree with him. That is why, instead of two low frequency oscillators, we started with a single crystal-controlled 1 MHz oscillator and took out the output along two different routes (Fig. 4). In one of them a 100 Hz sine wave was injected and by employing a single sideband generation technique[5], a 1 MHz+100 Hz signal was extracted. So now two different frequencies viz. one at 1 MHz and the other at 1.000100 MHz, appear at the two routes. Both are then fed to identical frequency dividers giving ultimate frequency division ratios of 1:40000. The outputs from these are rectangular waves having stable frequencies of 25 and 25.0025 Hz. The latter is shaped into sine waves[6] and, after power amplification, is made to drive the system under investigation.

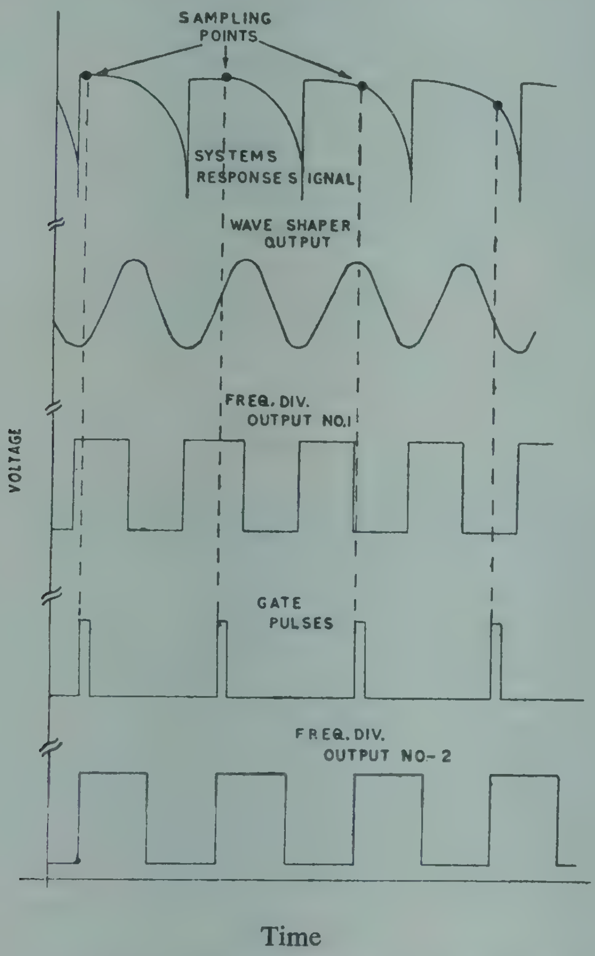
SAMPLING POINTS
SYSTEMS RESPONSE SIGNAL
WAVE SHAPER OUTPUT
FREQ. DIV. OUTPUT NO.1
GATE PULSES
FREQ. DIV. OUTPUT NO-2
VOLTAGE
Time

Fig. 2—Progression by Phase Shifting of Gate Pulse in the Present Method

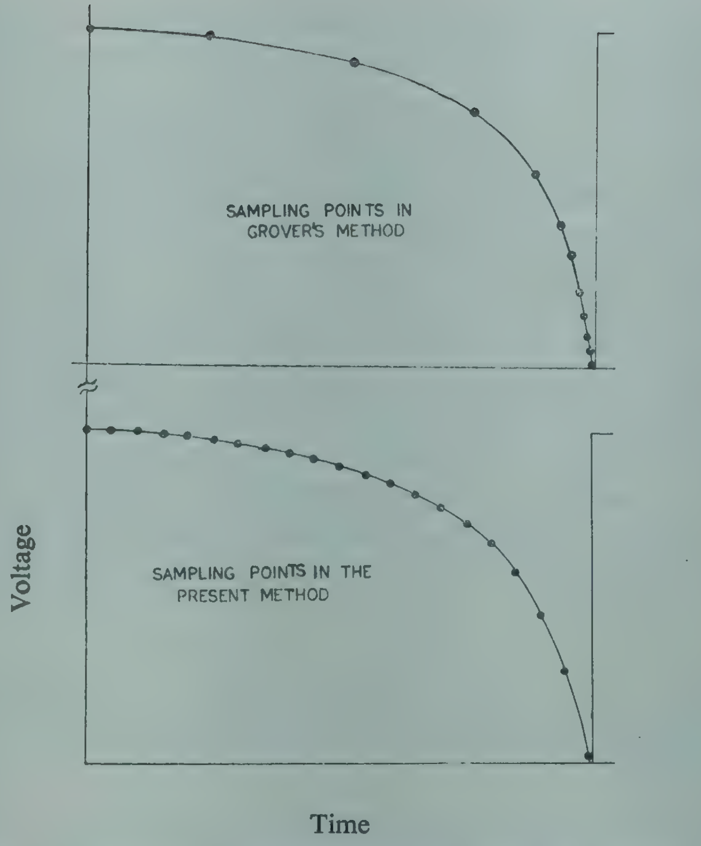

Fig. 3—Comparison of the Sample Points in the Two Methods

The gate pulses (Fig. 2) are derived from the lower frequency wave train (25 Hz). The waves are differentiated,

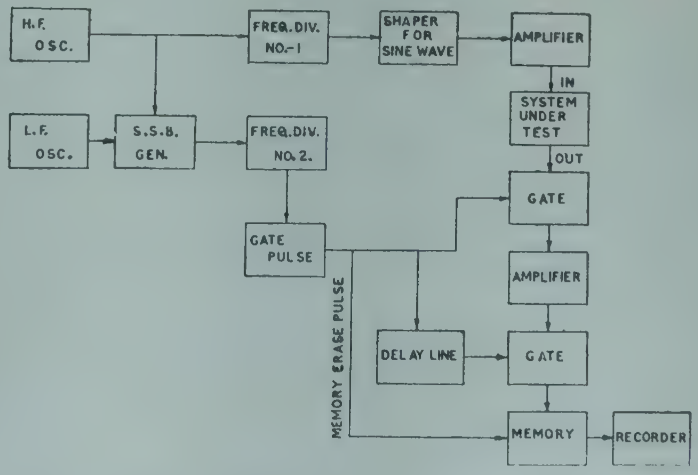
H.F. OSC.
FREQ. DIV. NO.-1
SHAPER FOR SINE WAVE
AMPLIFIER
IN
SYSTEM UNDER TEST
OUT
L.F. OSC.
S.S.B. GEN.
FREQ. DIV. NO. 2.
GATE
GATE PULSE
AMPLIFIER
MEMORY ERASE PULSE
DELAY LINE
GATE
MEMORY
RECORDER

Fig. 4—Block Diagram of the Complete Instrument

rectified and clipped to obtain the very narrow rectangular pulses required to drive the gate. All these simple operations are shown lumped together in the block labelled gate pulses in the block diagram (Fig. 4).

The gated or chopped signal is amplified by a wide-band AC amplifier. The amplified output is sent to the memory via a second gate circuit synchronized to open at the appropriate moment. The AC amplifier introduces a small delay in the path of the chopped signal. An equal delay is introduced in the path of the second gate pulse to achieve the synchronization. The delay is put to good use in the circuit. The undelayed pulse is utilized to erase the memory just before the new sample, which has suffered a delay, arrives at the memory gate. The recorder is connected to the memory unit via an impedance matching stage.

With the set up described, the 25.0025 Hz signal waveform will be traced out in 400 seconds, covering 10,000 sample points, a rate slow enough even for the slowest of recorders.

Acknowledgements

Thanks are due to Dr. B. K. Banerjee, Superintendent, Physical Research Wing, for his kind interest in the work. Sri S. N. Roye, Senior Technical Publications Officer, has permitted us an informal mode of presentation, which, we thought, would be more attractive, to scientists working in disciplines other than electronics, but who have to employ it as a tool.

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[Original mss. received on June, 3, 1972]

UDC 551-735.1:552.541 (545-8)

The pelletal limestone which forms a part of the Semri series has been studied from the petrogenetic point of view. The term pelletal cannot be applied as most of the so-called pellets show internal structure and also have a higher size range. Hence, they may be called Pisolitic limestone. The genesis of the limestone as well as the nature of the relationship between carbonate and chert apart from the various types of fabrics have been discussed in detail.

Petrogenesis of the Pelletal Limestones of the Semri Series of Lower Vindhyan Formation Around Chitrakot area in Banda District, Uttar Pradesh

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The lower Vindhyan rocks were studied in detail by the earlier workers in the different areas of Rajasthan and Mirzapur district of Uttar Pradesh. The Vindhyan rocks are known for their monotonous lithology without any major textural and mineralogical variation. A detailed microscopic study of the carbonate rocks is not possible because of their fine grained nature apart from post depositional changes, like diagenesis and dolomitization, in a few cases. In the present area, the pelletal limestone occurring within the Semri Series was selected for detailed study.

Location of the Area and Stratigraphy

The area investigated lies between 25°06′ and 25°15′ N latitude and 80°50′ to 81° longitude in and around Chitrakot, of Banda district (U.P.) and falls within the Survey of India Toposheet No. 63 C/16. On the basis of cursory investigation, Auden[1] established the following sequence for the area of the various localities for the Karwi area (Table 1). Ferruzudin[2] made preliminary palaeocurrent study of the arenites of Semri series.

Except for a cursory field description, no detailed

TABLE 1—SCHEMATIC TABLE FROM NORTH TO SOUTH THROUGH KOHI HILL (after Auden[1])

Chitrakot	Bihara 915 hill	Sangrampur 822 hill	Kohi 937 hill	Stage
Flaggy, current bedded, shaley sandstones 880 feet level	Flaggy shaley sandstones	Coarse and fine quartzites	Quartzites and sandstones	Kaimurs
Granite	Flaggy glauconitic beds	Flaggy glauconitic beds	Massive Tirohan limestone flaggy glauconitic beds	Semirs
	Pellet limestone	Pellet limestone	Pellet limestones	
			Limestone with glauconites	
	830 ft. level	755 ft. level	510 ft. level	
	Granite	Granite	Granite	

laboratory studies of the pelletal limestone, from the point of view of its genesis, have been reported.

Petrography

A good number of samples of the different types of pelletal limestones were collected with a view to examine the possibility of any phosphorites occurring in these rocks as these are associated with chert. But on chemical analysis, no phosphatic material was found. In the field, the pelletal limestone occurs as beds with very low dip, grading into bands of cherty glauconitic limestone without any sharp contact (Fig. 1). At the top also the aphanitic cherty limestone with conchoidal fracture is observed. The pelletal limestones are quite hard and form a marker horizon in the Chitrakot, Bihara, Kohi and Sangrampur hills.

The hand specimen (Fig. 2) definitely depicts certain interesting features which have a definite bearing on the genesis of these rocks. The sample was cut perpendicular to bedding plane and one of the faces was polished. In the polished face, it is possible to observe the textural features. There are subrounded intraclasts[3], which contain a lot of pellets that are cemented together. Both the pellets as well as intraclasts show dark reddish brown colour. According to Folk[3], intraclast is a fragment of more or less consolidated calcareous material, produced by erosion within the basin of deposition and redeposited there. In the present study, the intraclasts are of the size of nearly 3.5 cm. with an elliptical as well as sausage shape.

Microscopic Study

Eight thin sections were made from the various types of pelletal limestone and their modal composition was determined on the basis of 500 point counts. The framework of the rock was found mainly made up of pellets, detrital quartz and glauconites which are embedded in a carbonate as well as siliceous cement (Table 2).

Pellets: The framework's major constituent is the rounded grains, called by the earlier workers as pellets. According to earlier workers, the pellets must not have an internal structure, but in the present study (Fig. 3) they definitely have an internal structure. Their size is also more than 2 mm. They have beautiful concentric outer rims. The nucleus is absent except for the presence of very fine-grained reddish brown iron oxide. The relationship between the pellets and the cementing materials show that the former were brought from different sources. Due to rolling, the pellets have attained good roundness. The alternate concentric rims of iron oxide and white coloured microcrystalline calcite or chert show definitely various periods of changing climate (Fig. 4). The deformation of some pellets is mainly due to their transportation when they are in a semi-dry condition after the formation. The presence of detrital ferrugenous material in the pellets as embedded ones is also due to the movement in a semi-dry condition. While in movement, unequal enlargement has taken place due to plastic flow or deformation resulting in the irregular shape. Further consolidation and drying resulted in the coalescing of the interior which gave rise to desiccation cracks which are wider in the centre and narrower in the margins. Criss-cross desiccation cracks have also been observed (Fig. 5). At a later stage these cracks are filled with recrystallized material, and this nature indicates that the interior was not dry when the outer margin had become hard and compact. The pellets which are mainly calcareous in the earlier stages have been replaced by the cherty or ferrugenous material.

The interior of the pellets is made up of not any definite single mineral, but smaller ferrugenous pellets with irregular outline cemented together by calcareous or siliceous cement. It is possible to observe the gradual change in the colour and texture from core to the outer rim (Fig. 4). In certain cases, silicification has been observed. The size of the pellets varies from 2 mm. to

TABLE 2—MODAL COMPOSITION OF PELLETAL LIMESTONE

Section No.	Pisolites	Glauconites	Detrital Quatrz	Recrystallised Quartz	Rock Fragments	Chalcedony	Carbonate Cement
1.	63.2	1.5	3.2	2.2	—	7.2	22.6
2.	62.0	4.5	3.2	—	—	14.7	15.6
3.	47.4	10.6	6.0	—	—	7.8	28.2
4.	57.3	9.7	6.7	—	1.0	6.7	18.2
5.	41.4	4.2	—	—	—	0.2	54.2
6.	48.8	6.6	2.2	—	—	—	42.2
7.	61.0	4.2	7.2	—	—	1.0	26.6
8.	60.0	1.4	—	13.8	—	—	24.3

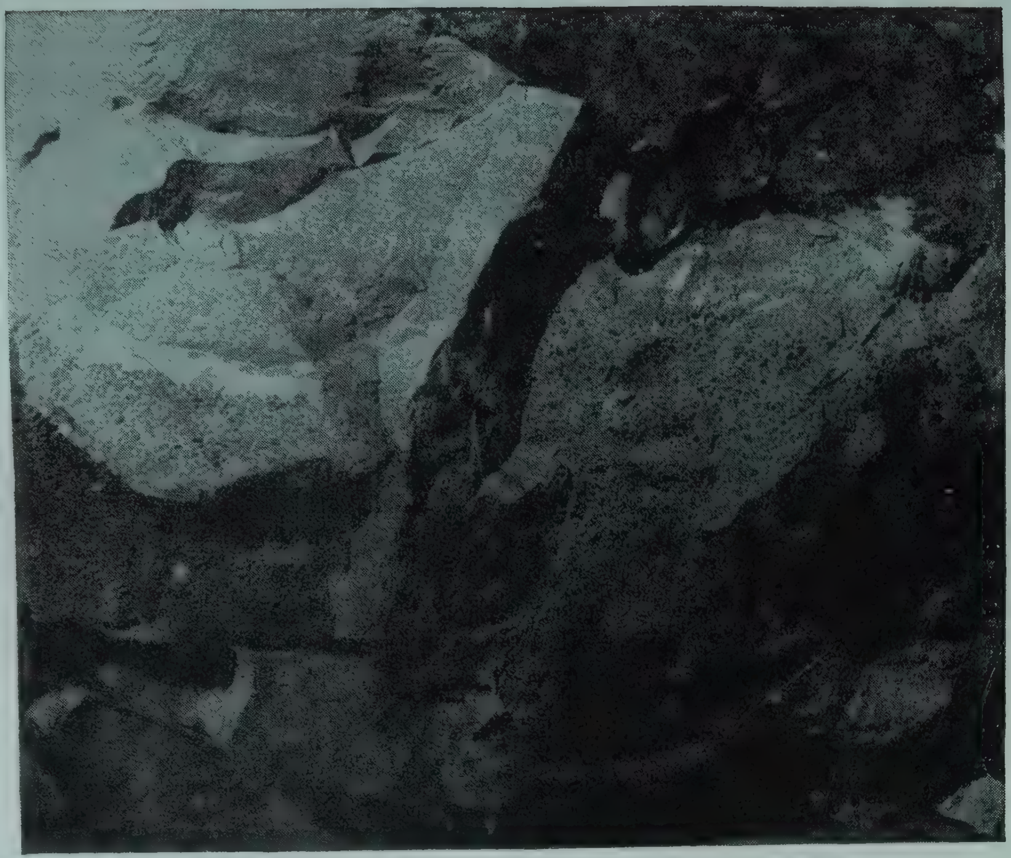

Fig. 1—Nature of Pisolitic Limestone

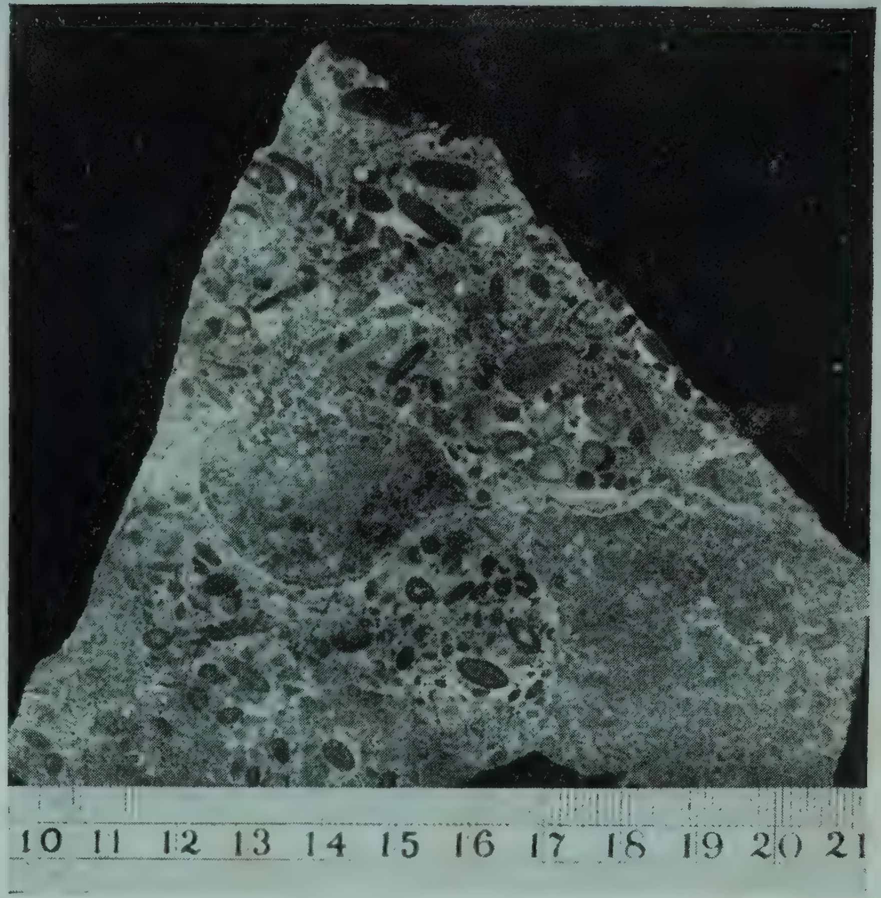
10 11 12 13 14 15 16 17 18 19 20 21

Fig. 2—Texture of Pisolitic Limestone (polished)

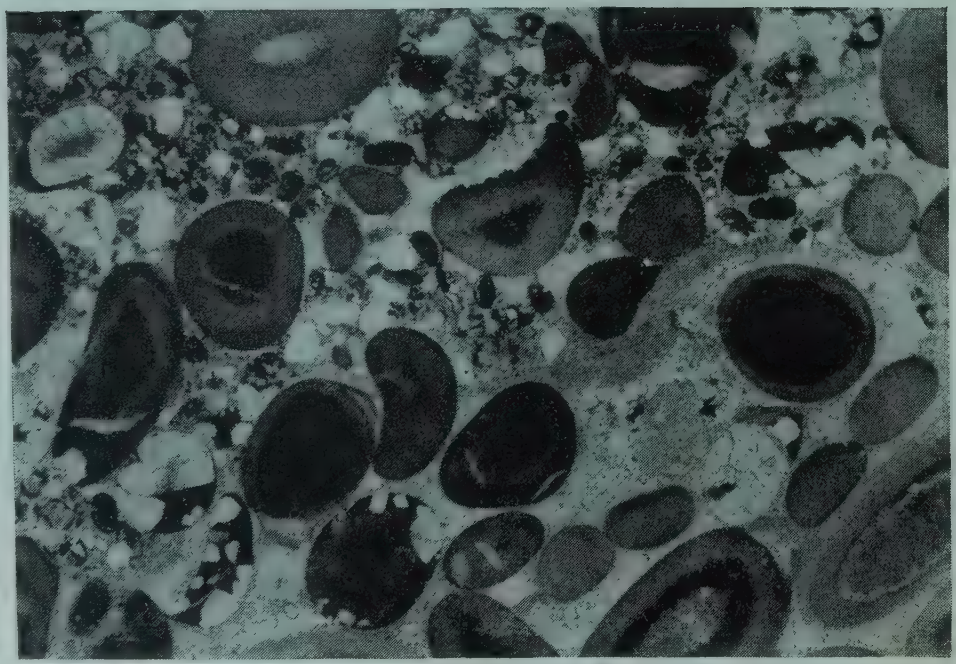

Fig. 3—Microscopic Features of the Pisolitic Limestone × 4

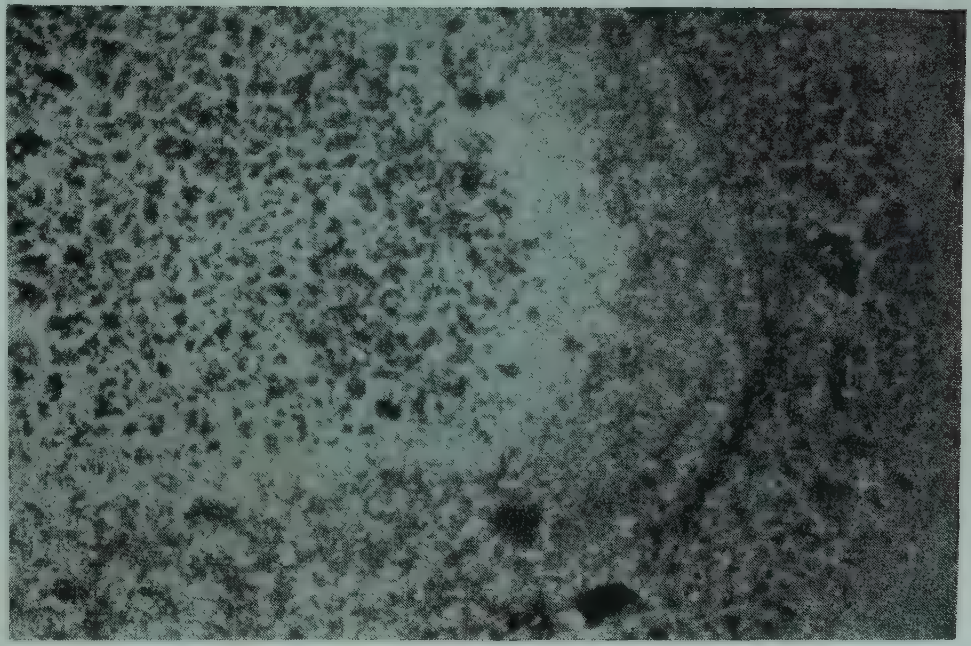

Fig. 4—Nature of the Variation of the Rims in the individual pisolite × 100 (crossed nicols)

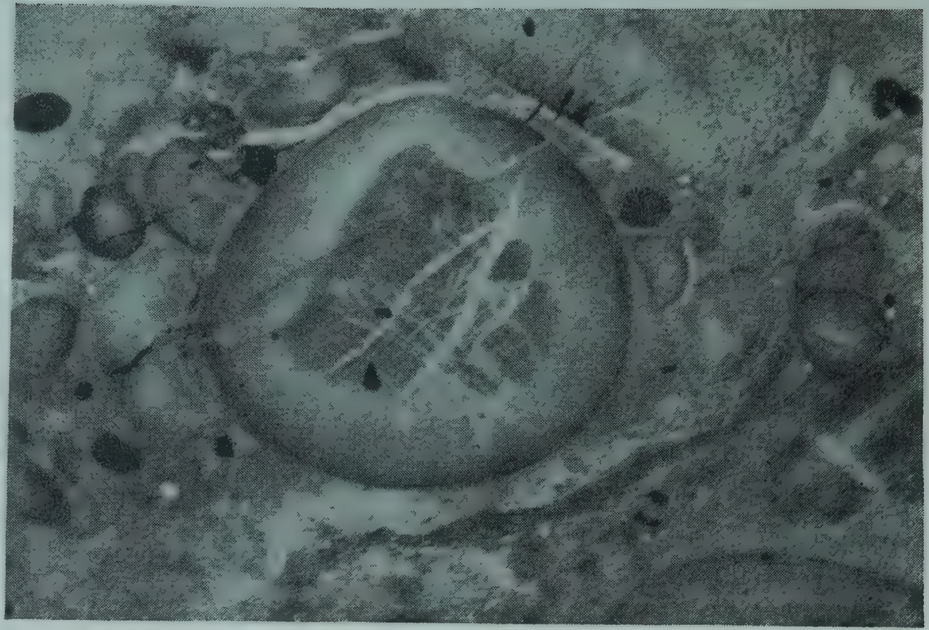

Fig. 5—Secondary Replacement of Pisolites × 5

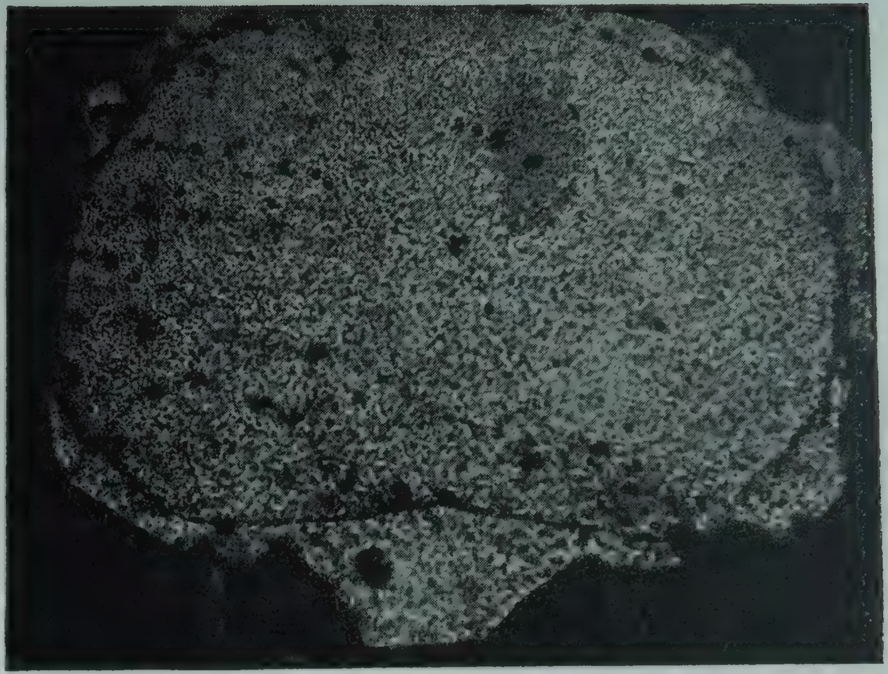

Fig. 6—Secondary Overgrowth of Quartz Grains (crossed nicols) × 83

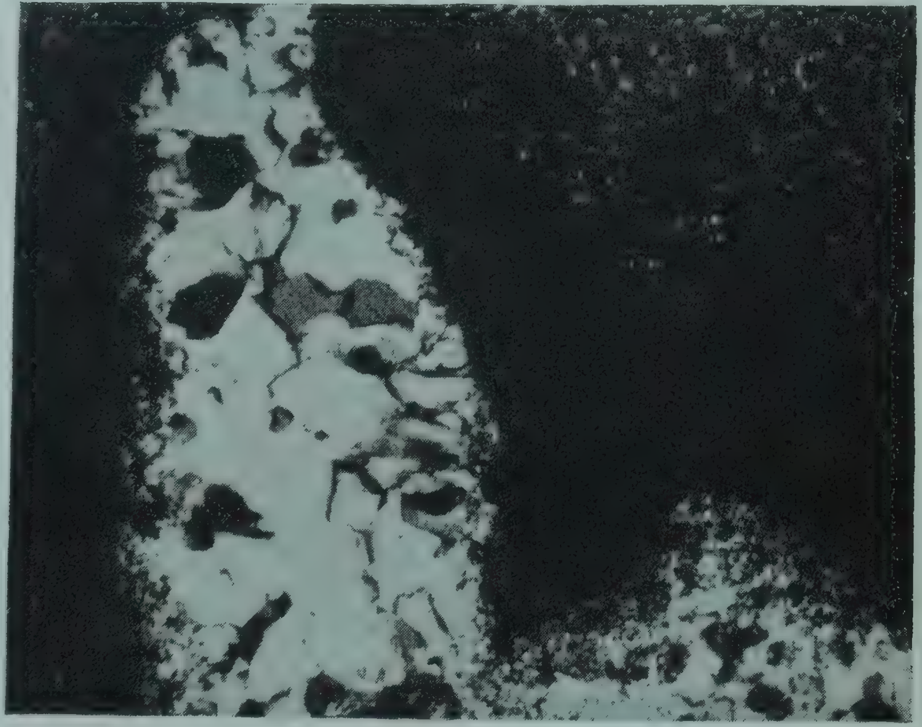

Fig. 7—Mosaic Quartz filling the Cracks (crossed nicols) × 64

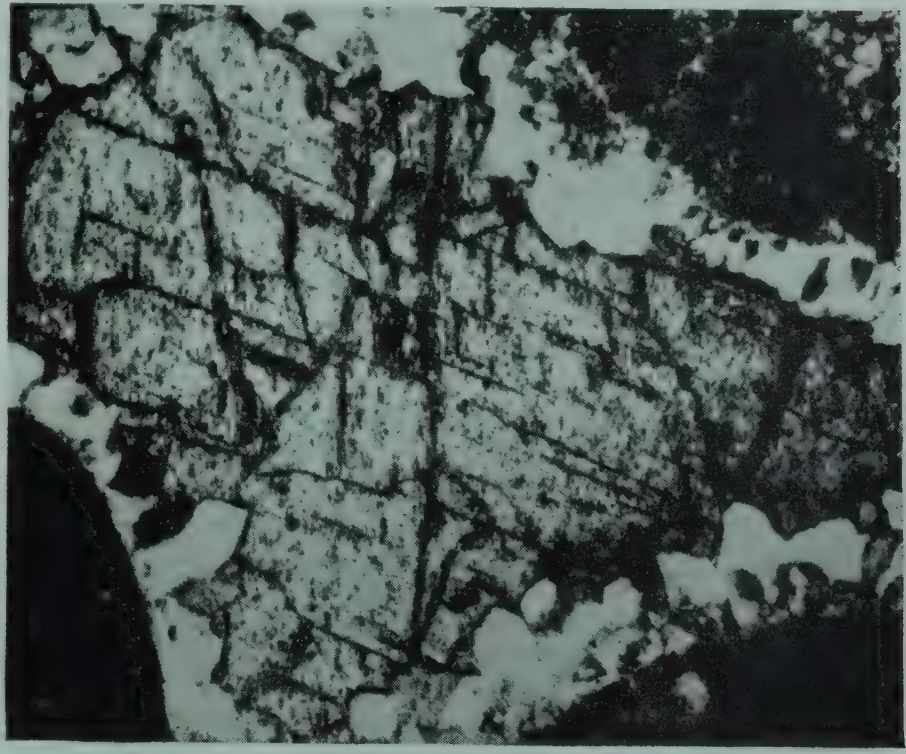

Fig. 8—Mosaic Quartz replacing Calcite (crossed nicols) × 64

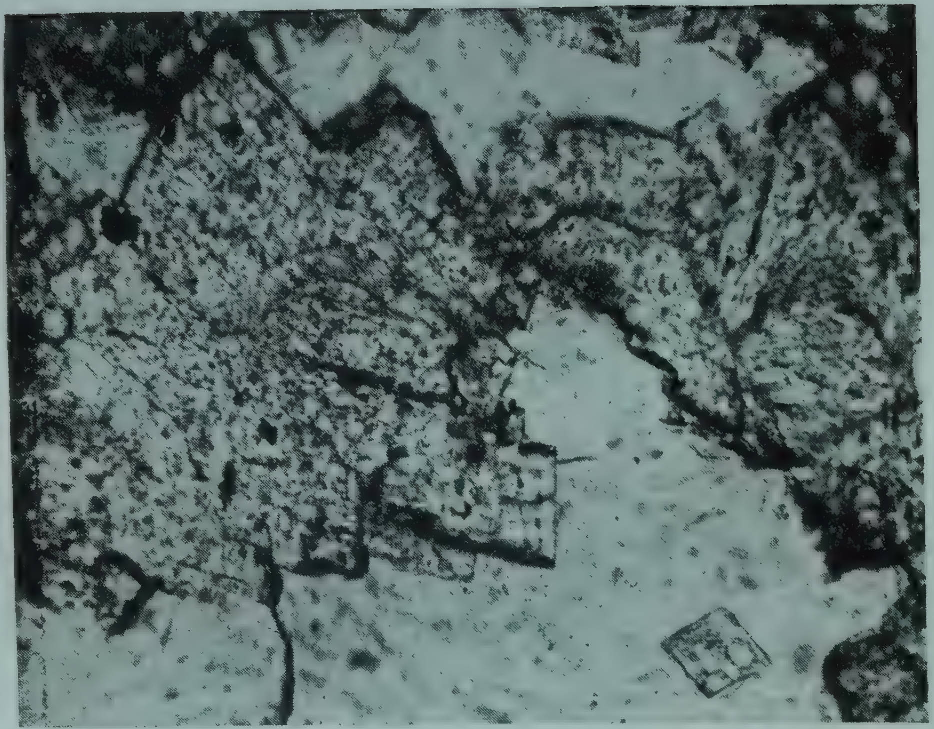

Fig. 9—Projection of Rhombic Calcite in the Silicious Matter × 100

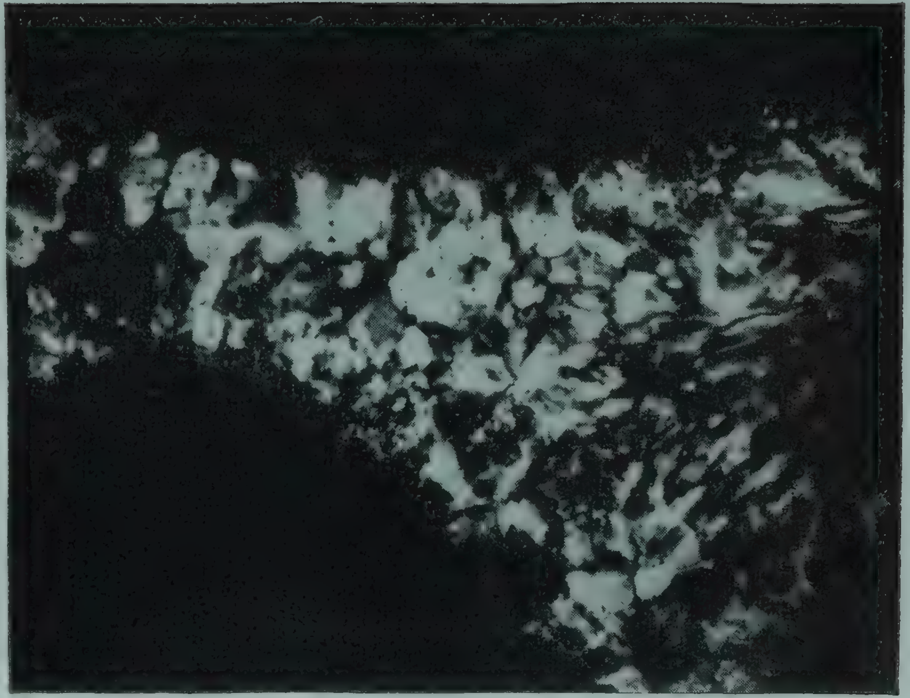

Fig. 10—Lateral Gradation of Chalcedonic Overlays into Mosaic Quartz (crossed nicols) × 32

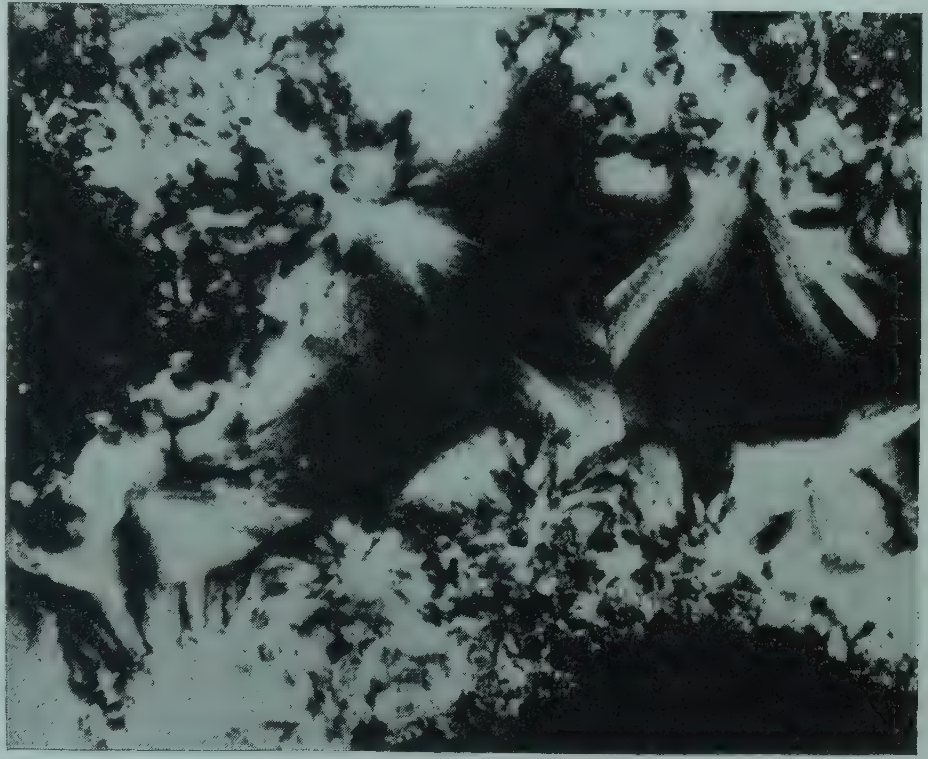

Fig. 11—Polygonal Spherulitic Chalcedony (crossed nicols) × 32

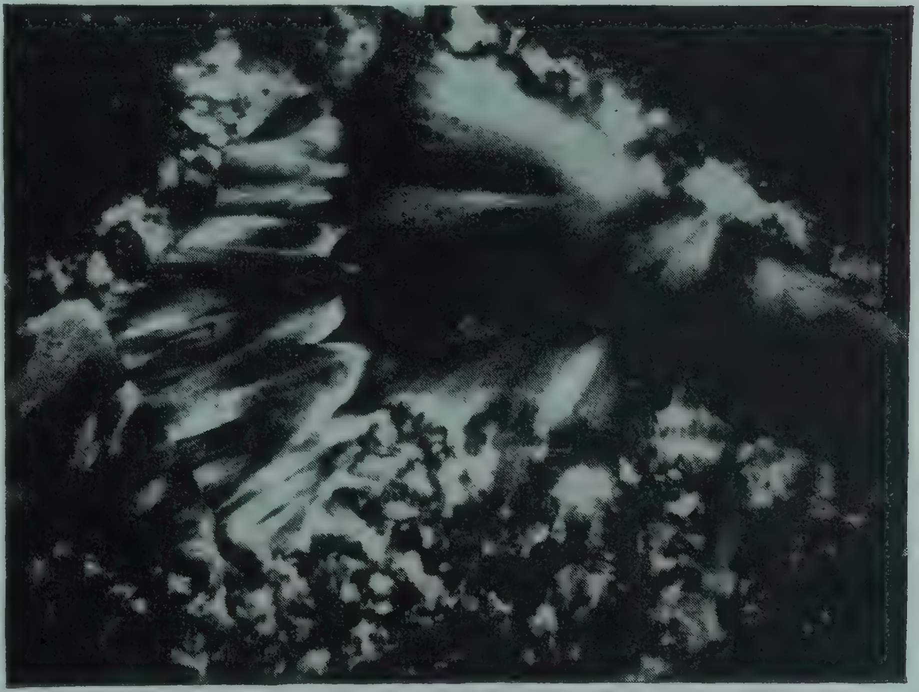

Fig. 12—Fan shaped Aggregate of Chalcedony × 32 (crossed nicols)

1 cm. These must be called pisolites and not pellets as they show a rim structure.

Glauconite: The glauconites also occur as very well-rounded pellets occupying the interspaces between bigger costitutents. The glauconite, quartz and calcite make composite grains. But the outer rim is very well-rounded.

The glauconite is also observed as replacing the bigger grains. Glauconitisation of the pisolites is quite a common phenomenon. In certain cases, the replacement is random while there are places where regular and uniform replacement has taken place from the outer margins of the pisolites (Fig. 5). Hence, it is possible to say that the glauconites are mainly of two generations, the one well-rounded and pelletal is detrital, while the other belonging to a later age has been formed *in situ* after the deposition of these pisolites. A more detailed study of the glauconite of the area is in progress in this laboratory and will be reported separately.

Detrital Quartz and Quartizite: Detrital quartz grains occur in a sporadic manner occupying the interspaces of bigger pellets. They are of the same size of the glauconite pellets. They are subangular to angular and their angularity is mainly due to corrosion by the carbonate cement. The detrital quartz grains are surrounded by chalcedonic material without any sharp boundary. There is also marginal replacement by glauconites and a few instances of secondary overgrowth on these quartz grains (Fig. 6) are observed. The overgrowth is in optical continuity with the primary one. The earlier generation of quartz is marked by a dusty ferrugenous rim.

The quartz grains belong to both varieties, viz. one showing sharp extinction and the other undulose extinction. A few well-rounded fragments of quartzites are also observed.

Cementing Material: The cementing material is recrystallized micrite as well as patches of sparry calcite showing corrosion of the detrital quartz grains. There are certain centres which sporadically show the development of secondary silica cement that has replaced the carbonate cement. The silicious cement is mainly made up of micro-crystalline quartz and fibrous chalcedony which can be called chert.

The five categories of silica fabrics, as described by Wilson[6] based broadly on the work of Walker[7], have been used in the present study. These are (a) mosaic quartz, (b) chalcedonic overlays, (c) spherulitic chalcedony, (d) lutecite, and (e) micro-crystalline granular quartz. In the present study, except lutecite, all the other fabrics are observed. The fabrics are described according to Wilson's[6] classification. The general grain shape, inter-grain relationship as well as the optical properties are the basis for the description.

Mosaic Quartz: The mosaic quartz is voidal filling, resembling drusy quartz. It is colourless and made up mainly of equigranular anhedral grains. There is a progressive increase from margin to the centre of the fabric (Fig. 7). This need not be ascribed as voidal growth of crystal into free spaces. In the same thin section, the tooth-like quartz grains project towards calcite (Fig. 8) in the centre, which is also very well crystallized with rhombohedral cleavage. So, it is possible to ascertain that the quartz has crystallized in the interspace between the calcite and the pellet. Due to later crystallization of silica, the calcite has developed some irregular fracture patterns.

The quartz grains generally show sharp extinction and the elongate grains that are perpendicular to the framework constituents are length slow in character.

Chalcedonic Overlays: This term is abbreviated by Wilson[6] from Walker's[7] term fibrous chalcedonic quartz overlay. It is colourless, with varying shades of brownish yellow. Under plane polarized light, the calcite rhombs are projecting as teeth towards this colourless mineral (Fig. 9). The calcite rhombs also contain inclusion. This fabric forms a rim around the allochems that are silicified. Laterally, they grade into mosaic as well as microcrystalline quartz. (Fig. 10).

Under crossed Nicols, the chalcedonic overlays appear fibrous. The extinction position is normal to the lateral extent of the overlay. Even by electron microscopic study (Folk and Weaver[8]), it was not possible to find evidence for the fibrous nature of this mineral. The fibres within these overlays show length fast character.

Spherulitic Chalcedony: The spherulites are colourless with varying shades of yellowish brown. The outer margin of each spherulite is either polygonal or circular (Fig. 11), producing a centred pseudo-uniaxial extinction figure observed mainly due to the orientation of the fibre. A sharp defined cross is only observed when the plane of the section passes through the centre of the spherulite. In many cases, when the growth was obstructed (Fig. 12), complete extinction cross is not developed with the result that fan-shaped aggregates are developed. There are various stages of spherulitic chalcedony development. Thus, Fig. 11 clearly shows two stages of development. Hence, it can be concluded that the availability of space is one of the deciding factors in determining the shape of spherulite.

The fibres are length fast. The spherulitic chalcedony grades laterally into chalcedonic overlays.

Microcrystalline Granular Quartz: It is colourless often showing patchy distribution. It is extremely fine-grained and often seen associated with all silica forms which laterally grade into micro-crystalline granular quartz. Under crossed nicols, an extremly fine-grained equigranular texture is observed except for the presence of one or two mosaic quartz grains.

Discussion

From the above detailed description, it is possible to conclude that these pellets are not pellets from the point of size and internal structure. These must be called pisolitic limestones, which have been brought from the adjacent source area. They were already ferrugenized. When these were deposited in the present area, there was some reworking resulting in the formation of intraclasts. Auden[1] has also come to the same conclusion: The pellets of silicified limestone sometimes occur very irregularly, as if they had rolled down a slope and become incorporated in the unconsolidated lime paste through the stirring up of the sea bottom by wave action. The pisolitic limestone is overlain by glauconitic sandstone, and massive Tirohan limestone. Hence, it can be seen that detrital materials, like silica and glauconites increased resulting in the formation of flaggy glauconite beds which show micro cross-lamination. The basin further deepened as indicated by the massive Tirohan limestone. Thus, a shallow agitated marine to calm and quite moderately deep water environment of deposition has been observed.

The silicification is of two stages. The pisolites with their silicified cores with a ferrugenized margin points to a predepositional silicification. The formation of the various silica fabrics after deposition in the cementing material is post-depositional silicification.

According to Folk and Weaver[8], the microcrystalline quartz results when crystal growth begins at very closely spaced numerous centres. The shape of the individual crystals depends upon the rate of growth in different directions. On the other hand, the chalcedonic quartz formation starts only at few centres. Thus undisturbed, continuous fibres are observed. Folk and Weaver[8] conclude that both the types can be formed by either direct precipitation or by replacement. In the present study, later precipitation in the voids is observed to be the main cause of secondary replacement.

The cherts are associated with carbonate rocks and hence they may be called calcareous cherts (Carozzi[9]). The important character of calcareous cherts, viz. presence of grains and rhombohedra of calcite as relics of replacement irregularly scattered in the cement is abundantly present in these rocks. The replacement affects the cementing material earlier than the framework constituents.

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[Original mss. received on Dec. 7, 1972]

UDC 631.41:546.18

Appreciable release of phosphorus from otherwise 'fixed' condition is observed in 10 days in five acidic soils (pH 4.70 to 6.20) of W. Bengal when treated with complexing agents, like EDTA, potassium humate, urea, oxalic, citric and salicylic acids. EDTA and humate are nearly 2 to 3 times as effective as the other reagents used and released 19 to 28 per cent of the total phosphorus. The relative efficiencies of the agents used is noted to be higher when the pH of the soil system was controlled at 6.5.

Release of Native Phosphates by Some Complexing Agents in Acidic Soils

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Presidency College, Calcutta

It is well established that in presence of anions that are capable of chelation with iron and aluminium, the availability of native phosphates increases in acidic soils. Organic anions, humus and lignin are capable of replacing phosphate from the iron and aluminium; the other similar reagents are ammonium fluoride, sodium arsenate, sodium hydroxide and citric acid[1]. Ghosal and Chakravarti[2] reported that phosphorus availability in acidic soils increases on treating them with chelating agents, like aluminon, oxine, N-benzoyl phenylhydroxylamine and humic acid. Since the chelating and complexing agents appear to be rather specific in the sense that they release phosphate from their combination with iron and aluminium, it is worth studying the effect of some more complexing agents on the native phosphates in the acidic soils and hence the present experiment was carried out.

Experimental

Soil samples were collected from the following agro-climatic regions of West Bengal: (i) hilly forest soil of Darjeeling; (ii) Gangetic alluvial soil of Karticpur (24-Parganas); (iii) lateritic soil of Chandrakona (Midnapur); (iv) lateritic soil of Mohammedbazar (Birbhum); and (v) Gangetic alluvial soil of Haringhata (Nadia) All the samples were collected from 0-15 cm. layer of virgin lands, covered by natural vegetation, adjacent to cultivated fields. The relevant data on some soil characteristics are given in Table 1. Mechanical analysis was carried out by the international pipette method[3], organic carbon by Walkly and Black's method and cation-exchange capacity by the neutral normal ammonium acetate method[4]. The native inorganic soil phosphate was fractionated by the method of Chang and Jackson[5] and data presented in Table 1.

The complexing agents used were EDTA, potassium

TABLE 1—PHOSPHATE STATUS AND SOME CHARACTERISTICS OF THE SOILS

Soil	Mechanical Composition, %			pH	Org. C, %	CEC, me/100g.	Total P, ppm	Al-P, ppm	Fe-P, ppm	Ca-P, ppm	Red Soil-P, ppm
	Sand	Silt	Clay								
Darjeeling	69	19	12	4.70	1.4	6	500	160	168	3	145
Karticpur	48	32	20	5.40	0.5	16	467	130	138	48	130
Chandrakona	69	13	18	5.70	0.6	10	340	80	60	40	150
Mohammedbazar	61	22	17	5.75	0.5	10	322	60	50	80	120
Haringhata	54	30	16	6.20	0.7	12	495	120	123	116	120

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*Present Address: Sr. Soil Chemist, FCI Ltd., Durgapur-12, W. Bengal humate, urea, citric, oxalic and salicylic acids. Potassium humate was prepared as follows: To the electrodialysed humic acid from Darjeeling soil, caustic potash solution was added drop by drop until the pH was about 8 and then the solution was concentrated to about 5 ml. To this concentrated solution, acetane and then alcohol was added when potassium humate precipitated. The precipitate was washed several times with 95 per cent alcohol to remove excess caustic potash. Potassium humate was redissolved in water and evaporated to dryness.

The experiment was set up with reagent-soil ratio 1:10 following Leaver and Russell[6]. 0.1 g. of each complexing agent and 1 g. of soil were taken in separate stoppered bottles and shaken thoroughly after adding 25 ml of water. After observing the pH of the suspension, a few drops of toluene were added to check the fungal action and then left for 10 days with occasional shaking. At the end of 10 days pH of the suspension was measured and then centrifuged to obtain a clear supernatant liquid. Phosphorus in the clear solution was determined by the chloromolybdic acid method[4].

A second set was prepared as above with the difference that pH of the suspension was maintained at 6.5 throughout the period under study by means of 0.05 N caustic potash and 0.05 N hydrochloric acid.

Results and Discussion

The results for phosphorus release from soils are given in Tables 2, 3 and 4.

Forms of Inorganic Phosphorus: The total inorganic phosphorus in the soils ranges from 322 to 500 ppm, highest being in Darjeeling soil and lowest in the lateritic soil of Mohammedbazar. The inorganic phosphorus exists mainly as iron phosphate, aluminium phosphate and reductant soluble phosphate (Table 1). The relative proportions of these forms are more or less the same in Darjeeling, Karticpur and Haringhata soils, but the percentage of reductant phosphorus in the two lateritic soils of Chandrakona and Mohammedbazar is markedly greater than that of iron phosphate and aluminium phosphate. It is revealed that the major part of native phosphate exist in iron and aluminium phosphate fractions that may liberate marked amounts of soluble phosphorus when acted upon by complexing and chelating agents.

Release of Native Phosphorus: Available phosphorus increased markedly in all cases in all the soils by the complexing and chelating actions of the reagents used (Table 4). EDTA and potassium humate are found to be nearly 2 to 3 times as effective as the other complexing and chelating actions of the reagents used (Table 4). EDTA and potassium humate are found to be nearly

TABLE 2—Change of pH in Soil Suspension and Release of Phosphorus in 10 Days

Treatment	Darjeeling			Karticpur			Chandrakona			Mohammedbazar			Haringhata		
	pH		P, ppm	pH		P, ppm	pH		P, ppm	pH		P, ppm	pH		P, ppm
	a	b		a	b		a	b		a	b		a	b	
Control	5.10	5.10	10	5.65	5.65	6	6.10	6.10	5	6.25	6.25	6	6.50	6.50	6
EDTA	5.05	6.10	100	4.90	6.40	100	4.65	6.36	80	5.10	6.50	86	5.10	6.30	100
Potassium humate	4.20	6.35	120	4.35	6.50	110	4.55	6.60	94	4.60	6.20	84	4.60	6.70	96
Urea	8.20	8.20	56	7.05	8.00	28	7.75	8.10	28	7.80	7.90	50	8.10	8.10	50
Oxalic Acid	2.05	5.30	60	2.30	5.80	28	2.10	6.20	45	2.35	6.40	54	2.50	6.70	62
Citric Acid	2.80	5.30	50	3.00	6.10	68	2.80	6.10	36	3.00	6.20	46	3.10	6.30	60
Salicylic Acid	2.70	5.10	54	2.80	5.60	56	2.65	6.20	45	2.90	5.80	40	3.05	6.20	52

a = initial b = final

TABLE 3—Release of Native Phosphorus at pH 6.5 by Complexing Agents, ppm

Treatment	Darjeeling	Karticpur	Chandrakona	Mohammed bazar	Haringhata
Control	14	10	8	8	6
EDTA	132	110	100	86	94
Potassium humate	140	100	90	90	110
Urea	56	40	48	45	44
Oxalic Acid	60	40	68	54	60
Citric Acid	56	80	56	54	54
Salicylic Acid	76	68	56	48	60

TABLE 4—RELEASE OF NATIVE PHOSPHORUS AS THE PERCENTAGE OF TOTAL PHOSPHORUS $\left(\frac{P_S}{P_T}\times 100\right)$

Treatment	Darjeeling		Karticpur		Chandrakona		Mohammedbazar		Haringhata	
	a	b	a	b	a	b	a	b	a	b
Control	2	3	1	2	1	2	2	2	1	1
EDTA	20	26	21	23	23	29	27	27	20	19
Potassium humate	24	28	23	21	27	26	26	28	19	22
Urea	11	11	6	8	8	14	15	14	10	9
Oxalic Acid	12	12	6	8	13	20	17	17	12	12
Citric Acid	10	11	14	17	10	16	14	17	12	11
Salicylic Acid	11	15	12	14	13	16	12	15	10	12

a=Uncontrolled pH b=pH 6.5

2 to 3 times as effective as the other complexing agents used. EDTA released 20 to 27 per cent of total phosphorus, the highest being Mohammedbazar soil (27 per cent) and lowest in Haringhata and Darjeeling soils (20 per cent). When pH is controlled, the release of phosphorus is increased substantially in Darjeeling, Karticpur and Chandrakona soils; no such increase is noted in Mohammedbazar and Haringhata soils. Phosphorus release is, however, maximum with potassium humate in Darjeeling, Karticpur and Chandrakona soils which release 23 to 27 per cent of total phosphorus at uncontrolled pH. In Mohammedbazar and Haringhata soils, EDTA is found to be slightly more effective than potassium humate. By controlling pH at 6.5 phosphorus availability decreased in Karticpur and Chandrakona soils, but increased in other three soils. Urea released 6 to 15 per cent of total phosphorus and is observed to be least effective amongst all the reagents used except in Mohammedbazar soil, where it is more effective than citric and salicylic acids. When pH is controlled, efficiency of urea remained more or less unaltered except in Chandrakona soil where a marked increase in available phosphorus is noted. About 6 to 17 per cent of total phosphorus is released by the complexing action of oxalic acid, the highest being in the lateritic soils of Mohammedbazar and lowest in Karticpur. The available phosphorus remained more or less unaffected by controlling pH except in Chandrakona soil, where about 20 per cent of total phosphorus is released at pH 6.5. Citric acid released about 10 to 17 per cent of total phosphorus and is found to be more effective at pH 6.5 in releasing phosphorus. Similar results are also obtained with salicylic acid.

The complexing agents are found to be comparatively more effective in the two lateritic soils of Chandrakona and Mohammedbazar (Table 3).

It is suggested that ligands of the complexing agents added reacted with the metal cations, viz. Fe^{3+}, Al^{3+}, Ca^{2+}, forming more stable complexes and release phosphate. The greater efficiencies of EDTA and potassium humate may be due to the fact that these two form more stable complexes with above cations than the other agents used.

Acknowledgement

The author's thanks are due to Dr. S. N. Chakravarti, Presidency College, Calcutta for his kind interest.

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[Original mss. received on Jan. 23, 1973]

UDC 631.47: 631.85: 632.12

Six phosphatic fertilizers, viz. single superphosphate, carbonitric and sulphonitric nitrophosphates, ammonium phosphate and Suphala 20:20:0 and 15:15:15 were applied (100 ppm phosphorus each) to 200 g. of sandy-loam soil (pH 6.80) at three water regimes, viz. 50 per cent maximum water holding capacity, saturation and submergence, and the available phosphate was estimated by the Oslen's method at 10 days' interval.

Ammonium phosphate and carbonitric nitrophosphate extracted significantly higher and lower available phosphate respectively compared to the other sources. However, no significant difference in the available phosphorus was discernible due to the sulphonitric nitrophosphate, Suphala 15:15:15 and single superphosphate. In general, a low availability of phosphate in the soil was associated with a higher percentage of citric acid-soluble phosphorus in the fertilizer.

During the experimental period a significant increase in the availability of phosphorus was noted up to the 30th day followed by a decline on the 40th day. Submergence significantly increased the availability of phosphorus over saturation and 50 per cent maximum water-holding capacity treatments.

The interaction between phosphate sources and time intervals was significant. However, the interactions between the other factors were non-significant.

Influence of Water Regimes and Time Intervals on the Availability of Phosphate from Different Sources*

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Introduction

Much has been reported on the comparative efficiency of various phosphates under upland conditions and the availability and solubility of native phosphates in flooded soils[1–5]. However, the concepts and generalizations drawn from research on upland soils may not be applicable in submerged soils since the transformation and availability of native and added phosphate changes with different soil moisture regimes[6]. In India, rice is grown under varied soil moisture conditions, viz. upland, alternate wetting and drying and continuous submergence, depending on the amount and distribution of rainfall. The management of phosphate fertility under these conditions also differs and becomes more complicated due to the uncertainties of monsoon and lack of sufficient irrigation facilities. In view of this, the present investigation was designed to have a quantitative estimate of the available phosphate from different phosphatic sources under controlled soil moisture regimes.

Experimental

The experiment was conducted with a sandy-loam soil from the plough layer (0-20 cm.) of the Agricultural Research Farm of the Planning and Development Division at Sindri. 200 g. (12 mesh) soil was taken in each of the 42 uniform size (500 ml. capacity) polyethylene bottles. The soil was treated separately with 100 ppm phosphorus from different sources of phosphates, viz. single superphosphate, carbonitric and sulphonitric nitrophosphates, ammonium phosphate, Suphala (20:20:0 and 15:15:15) and control. The water regime treatments were 50 per cent maximum water holding capacity (16.0 per cent moisture by weight), saturation and submergence (3 cm. level of water over the soil surface). During the experimental period these water regimes were maintained by daily

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* Presented at the 59th session of the Indian Science Congress held at Calcutta in February 1972.

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addition of water by adjusting the differences in weight due to loss of water. There were 21 treatment combinations and 2 replications. The bottles were arranged in a complete randomized block design under the laboratory conditions.

Periodic extraction of the available phosphate from the soil was made, taking samples at 10 days' interval, by the Olsen's 0.5 M sodium bicarbonate reagent[7] and determined colorimetrically by the chloro-stannous reduced molybdophosphoric blue colour method developed in hydrochloric acid system.[8]

The chemical properties of the soil used in the present investigation are given below:-

pH	6.80	
Electrical conductivity	0.70 m mho/cm at 25°C	
Organic carbon	0.705 per cent	
Available P	30 ppm	
Cation-exchange capacity	12.73 meq./100 g.	
Exchangeable Ca^{2+}	10.00 meq./100 g.	
,, K^+	0.26	,,
,, Na^+	0.13	,,
,, Mn^{2+}	0.02	,,
,, Fe^{2+}	0.10	,,

The pH and electrical conductivity of soil were determined by the usual methods at 1:2 soil: water ratio. Organic carbon and available phosphorus were estimated by the Walkey and Black's[9] and the Olsen's[7] methods respectively. The cation exchange capacity and exchangeable cations were determined according to Jackson[8].

Results and Discussion

The mean values of available phosphorus due to different phosphatic sources and time intervals averaged over water regimes are presented in Table 1.

Maximum availability of phosphate was obtained with ammonium phosphate (77.5 ppm) followed by Suphala 20:20:0 (69.9 ppm) which were significantly higher than all the other sources of phosphate fertilizers. Carbonitric nitrophosphate having all the phosphate in citrate-soluble form produced significantly a lower amount (50.0 ppm) of available phosphorus than all the other sources except control. However, no significant difference in the availability of phosphate was discernible among the sulphonitric nitrophosphate (61.8 ppm), Suphala 15:15:15 (60.8 ppm) and single superphosphate (60.1 ppm).

The result also indicated that, in general, the higher the percentage of citrate-soluble phosphate in the fertilizer, the lower the availability of phosphate in soil due to its application. This is clearly indicated from Figs. 1, 2 and 3 under 50 per cent maximum water holding capacity, saturation and submergence respectively. Carbonitric nitrophosphate containing 100 per cent citrate-soluble phosphorus gave minimum availability of phosphate, whereas ammonium phosphate having all its phosphate in water-soluble form gave maximum availability of phosphorus during the course of study in all the three water regimes. Sulphonitric nitrophosphate having 50:50 citrate-soluble and water-soluble phosphorus follow the medium course in the availability of phosphorus. These results are in conformity with the findings reported earlier[10].

The periodic observations of the phosphate extracted from the different treatments show significant increase in the availability of phosphorus up to the 30th day (36.8—88.2 ppm) followed by a decrease to 62.1 ppm on the 40th day.

TABLE 1—MEAN VALUES OF AVAILABLE PHOSPHORUS DUE TO PHOSPHATE SOURCES AND TIME INTERVALS

Phosphate Sources	Time Interval, days				Mean
	10	20	30	40	
Control	25.7	32.2	43.6	40.1	35.4
Single Superphosphate	39.3	52.8	91.4	56.8	60.1
Carbonitric Nitrophosphate	31.5	41.8	70.7	55.9	50.0
Sulphonitiric Nitrophosphate	38.2	51.4	95.1	62.5	61.8
Ammonium Phosphate	47.1	55.4	117.2	90.5	77.5
Suphala (20:20:0)	39.7	62.3	108.1	69.5	69.9
Suphala (15:15:15)	36.5	55.8	91.1	59.4	60.8
Mean	36.8	50.2	88.2	62.1	—

C.D. for phosphate means (marginal) at 5% level = 5.7
C.D. for time intervals means (marginal) at 5% level = 4.3
C.D. for phosphate × time intervals at 5% level = 11.5

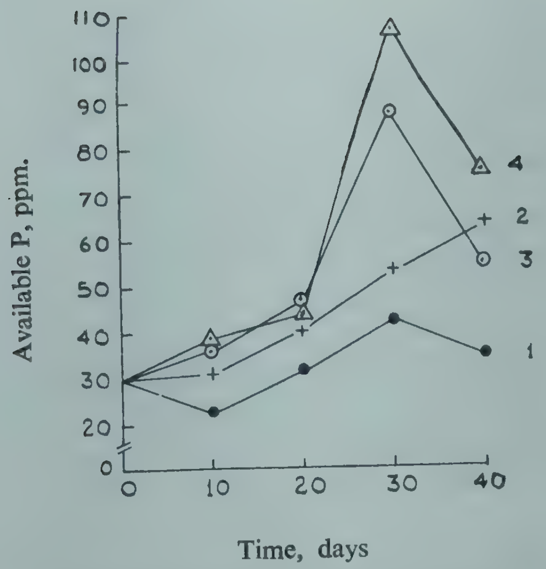

Fig. 1—Available Phosphorus due to Different Sources in Soil at 50% WHC

LEGEND (Figs. 1 and 2)

1. Control, 2. Carbonitric Nitrophosphate, 3. Sulphonitric Nitrophosphate, 4. Ammonium Phosphate

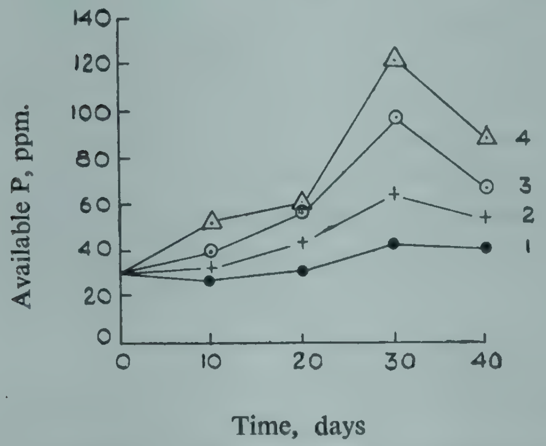

Fig. 2—Available Phosphorus due to Different Sources in Soil at Saturation

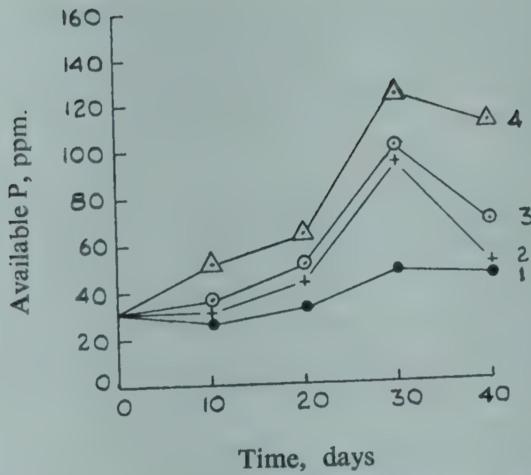

Fig. 3—Available Phosphorus due to Different Sources Under Submergence

1. Control, 2. Carbonitric Nitrophosphate 3. Sulphonitric Nitrophosphate, 4. Ammonium Phosphate

The interaction between phosphate sources and time intervals (Table 1) was significant. The highest availability of phosphate in soil due to all phosphate sources was noted on the 30th day and the lowest on the 10th day. In general, there was a significant increase in the available phosphorus with time up to the 30th day followed by a decline on the 40th day.

The mean values of available phosphorus due to the phosphate sources and water regimes averaged over the time intervals are presented in Table 2. With the increase in water level from 50 per cent maximum water-holding capacity to submergence of soil, there was a significant increase in the availability of phosphate from 53.3 to 65.3 ppm.

TABLE 2—MEAN VALUES OF AVAILABLE PHOSPHORUS DUE TO PHOSPHATE SOURCES AND WATER REGIMES

Phosphate Sources	Water Regimes			Mean
	*50% W.H.C.	Saturation	Submergence	
Control	32.5	35.0	38.7	35.4
Single Superphosphate	54.2	58.4	67.5	60.1
Carbonitric Nitrophosphate	47.0	48.6	54.3	50.0
Sulphonitric Nitrophosphate	56.0	65.2	64.1	61.8
Ammonium Phosphate	65.7	80.1	86.8	77.5
Suphala (20:20:0)	62.9	67.1	79.7	69.9
Suphala (15:15:15)	54.7	61.7	65.9	60.8
Mean	53.3	59.5	65.3	—

*50% of maximum water-holding capacity.

C.D. for water regimes means (marginal) at 5% level = 3.8
C.D. for phosphate means (marginal) at 5% level = 5.7
C.D. for phosphate × water regimes means = non-significant

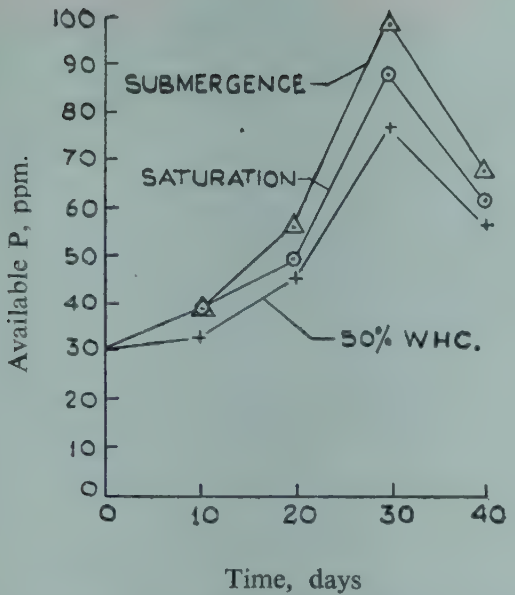

Fig. 4—Available Phosphorus in Soil due to Water Regimes as a Function of Time

The mean values of available phosphorus due to the water regimes at different time intervals are plotted in Fig. 4. The results show similar trend in the availability of phosphate during the course of experimental period under the three water regimes, but the increase in the level of water from 50 per cent maximum water-holding capacity to submergence markedly increased the amount of available phosphorus.

The interactions between phosphate sources × water regimes, water regimes × time intervals and phosphates × water regimes × time intervals were non-significant.

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[Original mss. received on Feb. 4, 1972]

UDC 631.4 (541.4): 631.85: 632.12

Investigation carried out to study the effect of water-logging on the available and inorganic phosphorus fractions of some typical soils of Bihar showed that the total reactive phosphates in soils decreased as a result of prolonged water-logging, although an increase was observed after 7 days. Calcium phosphate increased considerably after 7 days of water-logging in all the soils but decreased gradually on increasing the period of water logging. As a result of water-logging there was a net increase in calcium-phosphate fraction in the alkaline soils. After prolonged water-logging, saloid-bound phosphate, aluminium-phosphate and iron-phosphate decreased. Available phosphorus determined by Olsen, Bray's No. 1 and water-soluble phosphorus methods showed significant positive correlation with aluminium-phosphate and iron-phosphate but not with calcium-phosphate. After 60 days' water-logging, iron-phosphate and aluminium-phosphate did not show any significant correlation with Bray's No. 1 method but Olsen's method still showed significant positive correlation with these fractions. Water-soluble phosphorus showed significant positive correlation with all the reactive phosphates in water-logged soils.

Effect of Water-Logging on the Available Phosphorus and Inorganic Phosphate Fractions of Some Bihar Soils

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Introduction

Water-logged conditions bring considerable changes in the physico-chemical characteristics of soils. The availability of native phosphates in the water-logged soil is different from those in the air-dry soils[1]. It is, therefore, doubtful whether the soil rating done on the basis of results obtained from analysis of air-dry soil has any significance under water-logged conditions. At present there exists no reliable method of analysis for available nutrients in the water-logged soils. The transformations of various inorganic fractions of phosphates under water-logging conditions which affect the availability of the native phosphates in soil have not been studied carefully in this country. The present investigation was undertaken with a view to studying the effect of water-logging on the availability of soil phosphates in relation to the transformation of various inorganic phosphates in some representative paddy soils of Bihar.

Experimental

15 surface soil samples (0-25 cm.) from different agro-climatic regions of Bihar, with wide variations in soil reaction, were collected from cultivators' fields which usually do not receive phosphatic fertilizers. These were air-dried, powdered and screened through a 2 mm. sieve. Their mechanical analysis was done by the International Pipette method and the free calcium carbonate was estimated by rapid titration method[2]. Soil pH was determined in soil water suspension of 1:2·5 ratio using a pH meter equipped with glass calomel electrode. Phosphorus fractionation was carried out by the method of Chang and Jackson[3]; only first four fractions were included in this study and described as reactive phosphates. The total phosphorus was estimated in perchloric acid extract as described by Jackson[4]. The difference between the total and reactive phosphates is defined as less reactive phosphates. Available phosphorus was determined in water[5], Olsen[6] and Bray's[7] No. 1 extracts. Free ferric oxide was estimated by Mackenzie's method[8]. Incubation studies were carried out with 1g. of air-dry soil in test tubes maintaining 1 cm. of standing water throughout the experimental period[9]. The samples were analysed after

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7, 30 and 60 days' water-logging for various inorganic phosphate fractions. Available phosphorus was determined after 15 days' of water-logging. The results have been expressed on air-dry basis.

Normally for convenience, N ammonium chloride extracted phosphorus is reported as saloid-bound phosphate, 0.5N ammonium fluoride extracted phosphorus as aluminium-phosphate, 0.1N Sodium hydroxide extracted phosphorus as iron-phosphate and 0.5N sulphuric acid extracted phosphorus as calcium-phosphate and the sum of these fractions as total reactive phosphates. The same has been followed in this investigation.

Results and Discussion

The soils varied from sandy loam to heavy clay in texture, acidic to alkaline in reaction (pH varying from 4.9 to 8.7), free calcium carbonate ranged between 0.02 and 24.10 per cent, free ferric oxide varying between 0.23 and 1.75 per cent and organic carbon from 0.36 to 0.68 per cent (Table 1).

Effect of Water-logging on Available Phosphorus: Data on the available phosphorus of air-dry and water-logged soils are presented in Table 2. It may be seen that the available phosphorus of the same soil differed with different extractants, suggesting thereby the specificity of the extractants with regard to the different reactive phosphates in soil. All the three extractants clearly indicated that the available phosphorus status of most of these soils was low except Kishanganj soil. It is evident (Table 2) that the available phosphorus determined by Olsen and Bray's No. 1 methods increased in most of the soils as a result of water-logging, whereas water-soluble phosphorus did not show any appreciable change and in some cases appreciable reduction was observed. The increase in the available phosphorus of soil as a result of water-logging has been reported by Mandal[9], Islam and Elahi[10], Ekpeta and Cornfield[11], Chiang[12], Chiang[13,14] and Shapiro[15,16] who attributed such effect either to the decomposition of organic matter in soil liberating thereby carbon dioxide and organic acids or due to the reducing condition of soil due to flooding. Decrease in the water-soluble phosphorus may be caused by phosphorus sorption by the unsaturated surface layer[17] or due to transformation into water-insoluble iron, aluminium and calcium phosphate compounds as a result of water-logging.

Effect of Water-logging on the Inorganic Phosphate Fraction of Soil: The inorganic phosphate fractions of

TABLE 1—IMPORTANT SOIL CHARACTERISTICS

Sl. No.	Location	pH	Organic Carbon, %	Free CaCO$_3$, %	Free Fe$_2$O$_3$, %	Texture
1.	Kishanganj	4.9	0.46	0.01	0.54	Loam
2.	Araria	5.2	0.38	0.01	0.57	Sandy loam
3.	Khunti	5.3	0.65	0.082	1.29	Clay loam
4.	Kanke	5.7	0.39	0.086	1.78	Sandy loam
5.	Hazaribagh	5.7	0.38	0.08	1.33	Medium clay
6.	Ramgarh	5.9	0.40	0.02	0.94	Sandy clay loam
7.	Putida Yellow	6.7	0.61	0.02	0.23	Clay loam
8.	Danapore	7.0	0.63	0.01	1.51	Heavy clay
9.	Giridih	7.3	0.47	0.02	1.75	Sandy clay loam
10.	Tatanagar	7.3	0.45	0.02	0.33	Loam
11.	Darbhanga	7.8	0.38	0.03	0.69	Loam
12.	Samastipur	8.1	0.41	21.30	0.31	Loam
13.	Mithapur	8.1	0.68	0.40	1.49	Heavy clay
14.	Mushari	8.6	0.36	24.10	0.39	Clay loam
15.	Muradpur	8.7	0.29	3.90	0.87	Clay loam

TABLE 2—Available P_2O_5 in Air-Dry and Water-Logged Soils, ppm

Sl. No.	Location	Treatment	Olsen P	Bray's No. 1-P	Water-soluble P
1.	Kishanganj	Air-dry soil	59.0	84.0	11.5
		Water-logged soil	114.0	97.1	5.6
2.	Araria	Air-dry soil	15.8	7.2	2.1
		Water-logged soil	22.0	21.4	1.3
3.	Khunti	Air-dry soil	5.3	1.9	0.8
		Water-logged soil	14.0	0.5	0.5
4.	Kanke	Air-dry soil	6.2	4.7	4.8
		Water-logged soil	10.0	9.5	2.0
5.	Hazaribagh	Air-dry soil	5.0	1.0	3.2
		Water-logged soil	7.8	tr	0.8
6.	Ramgarh	Air-dry soil	12.3	3.1	4.0
		Water-logged soil	16.0	11.9	1.5
7.	Putida Yellow	Air-dry soil	6.2	1.2	0.3
		Water-logged soil	8.0	2.9	2.0
8.	Danapore	Air-dry soil	25.5	15.6	4.8
		Water-logged soil	71.0	21.4	6.4
9.	Giridih	Air-dry soil	5.3	0.7	1.1
		Water-logged soil	6.0	tr	tr
10.	Tatanagar	Air-dry soil	5.3	2.2	1.6
		Water-logged soil	3.0	1.0	1.3
11.	Darbhanga	Air-dry soil	1.8	6.0	1.3
		Water-logged soil	16.0	27.6	1.8
12.	Samastipur	Air-dry soil	4.4	tr	4.0
		Water-logged soil	15.0	1.0	3.1
13.	Mithapur	Air-dry soil	24.6	11.3	14.4
		Water-logged soil	94.0	22.8	5.1
14.	Mushari	Air-dry soil	9.7	0.7	3.2
		Water-logged soil	12.0	4.8	4.9
15.	Muradpur	Air-dry soil	3.5	tr	1.6
		Water-logged soil	2.0	0.5	2.0

air-dry soil as well as the transformations of these fractions due to water-logging is presented in Table 3 and plate No. 1 for acid soils and in Table 4 and plate No. 2 for neutral and alkaline soils. It may be seen that calcium-phosphate constituted the major bulk of the reactive phosphates in neutral and alkaline soils whereas iron-phosphate dominated in acid soils. Similar observations have been made by Banerjee and Mandal[18], Chiang[12] and Chiang[14] in water-logged acid and alkaline soils. It is also evident from the data (Tables 3 & 4) that the total reactive phosphate increased after 7 days of water-logging but decreased gradually as a result of prolonged water-logging in all the soils except in one or two exceptions.

Such increase is mainly due to the increase in calcium-phosphate fraction followed by a slight increase in aluminium-phosphate and iron-phosphate fractions in some acid soils. According to Chiang[13] the changes in pH, Eh, iron, and available phosphorus are very significant

TABLE 3—EFFECT OF WATER-LOGGING ON THE INORGANIC PHOSPHATE FRACTIONS IN ACID SOILS, ppm

Sr. No.	Soil	Treatment	Saloid-bound P	Al-P	Fe-P	Ca-P	Total Reactive P (Saloid-bound P + Al-P+Fe-P+ Ca-P)	Less Reactive P	Total P
1.	Kishanganj	Air-dry soil	0.8	105.5	111.7	45.6	263.6	764.9	1028.5
		Water-logged soil							
		(a) 7 days	0.5	110.2	95.6	85.0	291.3	737.2	
		(b) 30 days	2.1	44.0	140.4	65.2	251.7	776.8	
		(c) 60 days	tr	16.4	121.0	53.5	190.9	837.6	
2.	Araria	Air-dry soil	tr	24.4	48.2	126.7	199.3	443.5	642.8
		Water-logged soil							
		(a) 7 days	0.9	38.9	37.8	169.3	246.9	395.9	
		(b) 30 days	1.1	19.0	33.8	130.0	183.9	458.9	
		(c) 60 days	0.8	4.6	32.1	106.4	143.9	498.9	
3.	Khunti	Air-dry soil	tr	30.0	71.8	4.4	106.2	436.6	542.8
		Water-logged soil							
		(a) 7 days	0.3	15.1	59.3	41.1	115.8	427.0	
		(b) 30 days	1.3	13.0	73.8	15.0	103.1	439.7	
		(c) 60 days	tr	2.7	41.0	16.8	60.5	482.3	
4.	Kanke	Air-dry soil	tr	13.3	28.7	12.2	54.2	302.9	357.1
		Water-logged soil							
		(a) 7 days	tr	35.6	7.4	40.0	83.0	274.1	
		(b) 30 days	tr	9.0	20.5	8.7	38.2	318.9	
		(c) 60 days	tr	4.6	15.3	13.6	33.5	323.6	
5.	Hazaribagh	Air-dry soil	0.5	8.9	26.7	12.8	48.9	165.4	214.3
		Water-logged soil							
		(a) 7 days	0.8	12.1	22.2	14.4	49.5	164.8	
		(b) 30 days	0.8	10.0	15.4	20.0	46.2	168.1	
		(c) 60 days	tr	6.4	5.3	10.6	22.3	192.0	
6.	Ramgarh	Air-dry soil	tr	21.1	42.0	28.9	92.0	293.7	385.7
		Water-logged soil							
		(a) 7 days	tr	14.0	31.1	47.8	92.9	292.8	
		(b) 30 days	0.8	13.3	27.7	27.8	69.6	316.1	
		(c) 60 days	tr	11.8	18.9	18.7	49.4	336.3	
7.	Putida Yellow	Air-dry soil	1.3	28.9	54.3	21.1	105.6	437.2	542.8
		Water-logged soil							
		(a) 7 days	0.5	7.6	34.1	24.4	66.6	476.2	
		(b) 30 days	0.8	11.0	57.4	14.0	83.2	459.6	
		(c) 60 days	tr	2.7	30.5	12.9	46.1	496.7	

immediately after flooding, but gradually slackened after one week, becoming slow after 5 weeks and almost disappearing after 2 months. Since the favourable effects of water-logging do not persist long[13], considerable decrease in calcium-phosphate, aluminium-phosphate and iron-phosphate was observed as a result of prolonged water-logging which ultimately resulted in a low amount of total reactive phosphate in all the soils. It appears that as a result of water-logging there is a gradual transformation of iron-phosphate and aluminium-phosphate either into reactive calcium-phosphate or into less reactive phosphate such as occluded iron and aluminium phosphates, which are unavailable[19]. After prolonged water-logging even the reactive calcium-phosphate gets transformed into less reactive phosphate, possibly due to accummulation of organic acids[14]. It may be mentioned here that alkaline (calcareous) soils having pH above 8 showed comparatively higher amount of calcium-phosphate than the original soil even after prolonged period of water-logging. This has also been observed in

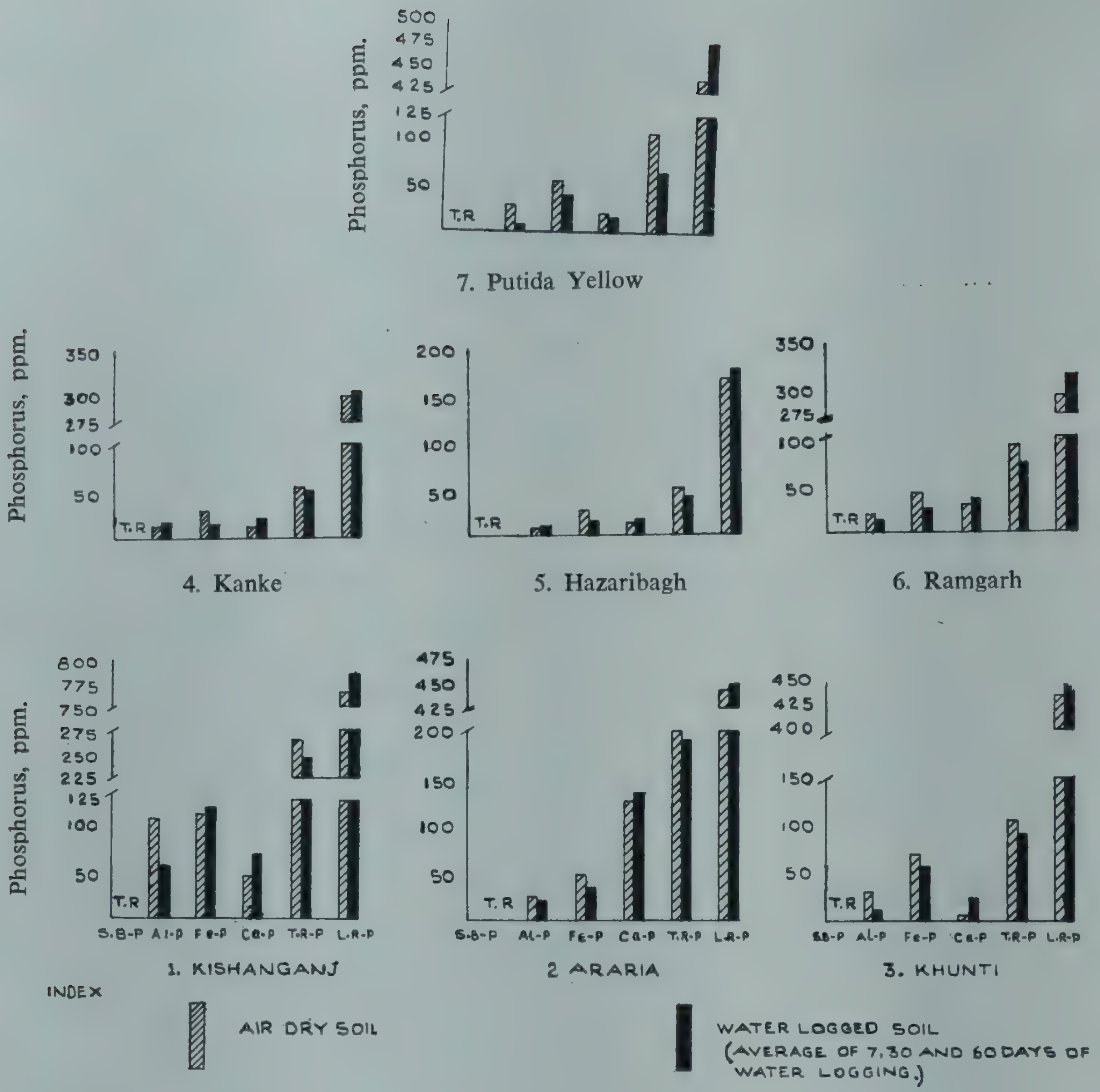


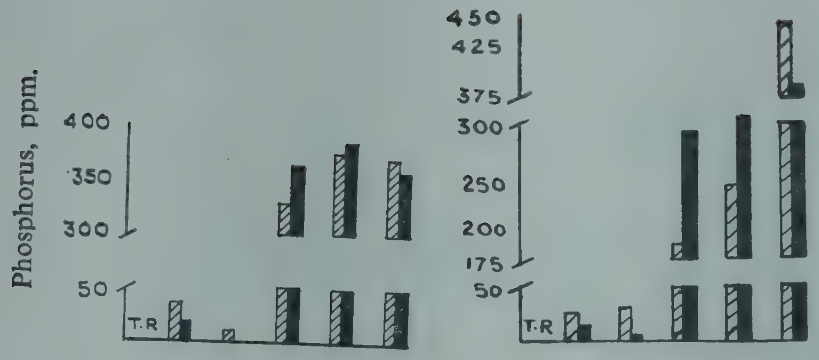
Fig. 1—Effect of Water-logging on the Inorganic Phosphate Fractions in Acid Soils.

S.B-P Saloid-bound P
Al-P Aluminium P
Fe-P Iron P
Ca-P Calcium P
TR-P Total Reactive P
LR-P Less Reactive P

Danapur soil (neutral), Kishanganj, Khunti and Kanke (acid) soils. The saloid-bound phosphate, however, did not show any definite trend after initial stages of water-logging but after 60 days only traces of it were observed in all the soils suggesting thereby that the transformation reactions attained a stable state.

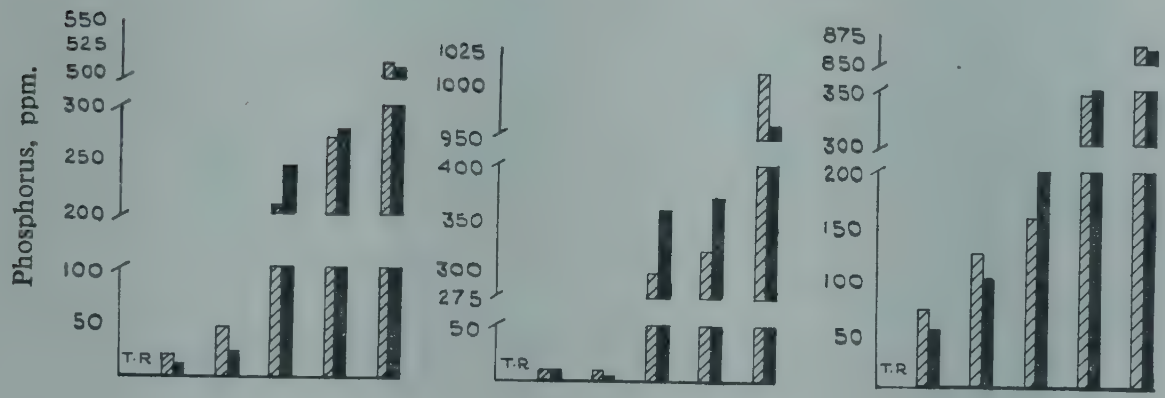
Relationship between the Available Phosphorus and Inorganic Phosphate Fractions: The data (Table 5) reveal that in air-dry soils available phosphorus, extracted by Bray's No. 1 and water-soluble phosphorus, is significantly correlated with aluminium-phosphate and iron-phosphate. In most of the soils under study, calcium-phosphate constituted the major bulk of the reactive inorganic phosphate fraction; however, calcium-phosphate did not show any significant correlation with the available phosphate suggesting thereby that only a small fraction of calcium-phosphate constitutes to the available phosphorus content while iron-phosphate and aluminium-phosphate although constituting comparatively smaller fraction of the reactive phosphates in these soils contribute much to the available phosphorus content.

In water-logged soils correlation coefficient between the available phosphorus and the different inorganic reactive phosphates (Table 6) reveal that even under water-logged condition aluminium-phosphate and iron-phosphate show significant positive correlation with the available phosphorus extracted by Olsen and Bray's No. 1 methods. Grigg[20] has also reported that Olsen and Bray's No. 1 extractants extract mainly aluminium-phosphate. After prolonged water-logging, phosphorus extracted by



7. Mushari

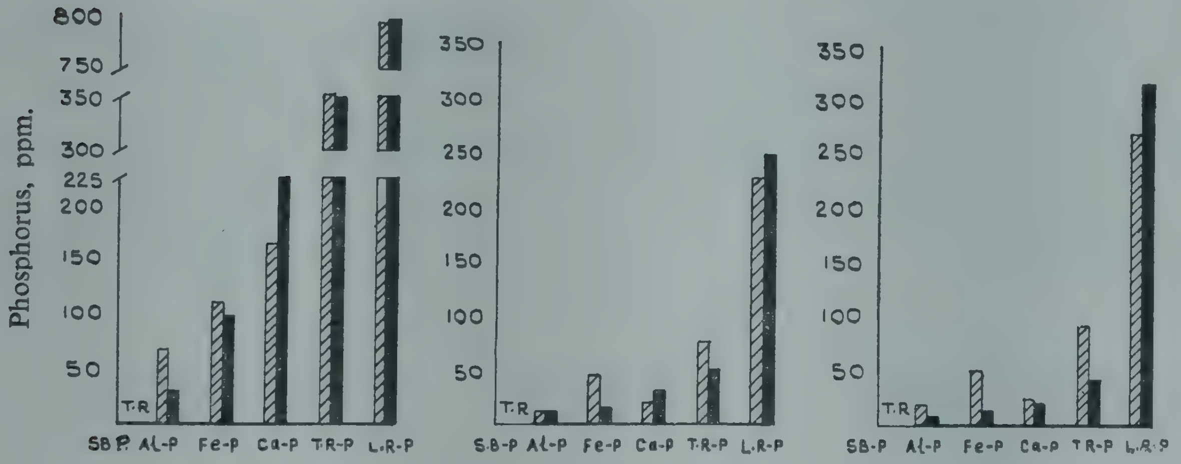
8. Muradpur



4. Darbhanga

5. Samastipur

6. Mithapur



1. Danapur

2. Giridih

3. Tatanagar

INDEX: SAME AS FOR FIG. 1.

Fig. 2—Effect of Water-logging on the Inorganic Phosphate Fractions in Neutral and Alkaline Soils.

S. B-P Saloid-bound P
Al-P Aluminium P
Fe-P Iron P
Ca-P Calcium P
TR-P Total Reactive P
LR-P Less Reactive P

Bray's No. 1 method did not show any significant correlation with aluminium-phosphate and iron-phosphate; however, phosphorus extracted by Olsen method shows significant positive correlation with aluminium-phosphate and iron-phosphate which strongly suggest that Olsen's extractant extracts considerable amount of aluminium-phosphate and iron-phosphate in water-logged soils.

As a result of water-logging aluminium-phosphate and iron-phosphate fractions became exceedingly soluble and these constitute the major bulk of the plant available phosphorus in water-logged soils[21], and in the absence of any plant these fractions undergo transformation into less reactive phosphates. Water-soluble phosphorus showed significant positive correlation with all the fractions of reactive phosphates suggesting thereby that a fraction of reactive phosphate remains in water-soluble

TABLE 4—EFFECT OF WATER-LOGGING ON THE INORGANIC PHOSPHATE FRACTIONS IN NEUTRAL AND ALKALINE SOILS, ppm

Sr. No.	Soil	Treatment	Saloid-bound-P	Al-P	Fe-P	Ca-P	Total reactive-P (Saloid-bound-P+ Al-P+Fe-P+ Ca-P)	Less reactive P	Total P
1.	Danapore	Air-dry soil	1.5	65.5	119.6	164.4	351.0	791.8	1142.8
		Water-logged soil							
		(a) 7 days	1.2	38.9	86.7	238.7	365.5	777.3	
		(b) 30 days	1.5	24.0	113.8	243.5	382.8	760.0	
		(c) 60 days	tr	17.3	92.6	190.3	300.2	842.6	
2.	Giridih	Air-dry soil	0.5	10.9	44.1	18.1	73.6	226.4	300.0
		Water-logged soil							
		(a) 7 days	tr	10.0	24.5	50.0	84.5	215.5	
		(b) 30 days	1.1	12.0	10.3	22.6	46.0	254.0	
		(c) 60 days	tr	9.1	2.7	11.8	23.6	276.4	
3.	Tatanagar	Air-dry soil	0.8	16.7	50.2	22.2	89.9	267.2	357.1
		Water-logged soil							
		(a) 7 days	0.9	5.4	22.2	30.0	58.5	298.6	
		(b) 30 days	2.1	9.0	11.8	16.7	39.6	317.5	
		(c) 60 days	tr	5.5	4.2	12.3	22.0	333.1	
4.	Darbhanga	Air-dry soil	0.4	18.9	43.1	206.7	269.1	516.6	785.7
		Water-logged soil							
		(a) 7 days	tr	17.3	21.5	288.6	327.4	458.3	
		(b) 30 days	1.1	10.0	26.7	218.8	256.6	529.1	
		(c) 60 days	tr	4.6	17.9	222.5	245.0	540.7	
5.	Samastipur	Air-dry soil	2.3	7.8	9.2	297.8	317.1	1011.4	1328.5
		Water-logged soil							
		(a) 7 days	1.1	6.5	3.7	366.3	377.6	950.9	
		(b) 30 days	2.1	6.0	tr	360.9	369.0	959.5	
		(c) 60 days	2.9	14.6	tr	335.4	352.9	975.6	
6.	Mithapur	Air-dry soil	0.8	69.9	123.0	154.4	348.1	866.1	1214.2
		Water-logged soil							
		(a) 7 days	1.2	57.8	96.3	227.6	382.9	831.3	
		(b) 30 days	2.9	78.3	99.4	181.3	361.9	852.3	
		(c) 60 days	2.3	20.0	95.7	190.3	308.3	905.9	
7.	Mushari	Air-dry soil	0.7	35.5	11.3	326.6	374.1	368.7	742.8
		Water-logged soil							
		(a) 7 days	3.7	20.5	tr	399.6	423.8	319.0	
		(b) 30 days	1.7	28.0	tr	355.0	384.7	358.1	
		(c) 60 days	3.2	8.2	tr	335.4	346.8	396.0	
8.	Muradpur	Air-dry soil	2.6	25.5	28.7	186.5	243.5	442.2	685.7
		Water-logged soil							
		(a) 7 days	0.9	16.2	6.7	310.0	333.8	351.9	
		(b) 30 days	0.9	18.2	5.1	295.0	319.2	366.5	
		(c) 60 days	0.5	6.4	tr	267.7	274.6	411.1	

TABLE 5—CORRELATION COEFFICIENT BETWEEN VARIOUS FORMS OF INORGANIC PHOSPHATE AND AVAILABLE P_2O_5 IN AIR-DRY SOILS, ppm

Available P_2O_5	Saloid-bound P	Al-P	Fe-P	Ca-P
Olsen P	−0.04	+0.92**	+0.73**	−0.07
Bray's 1-P	−0.02	+0.83**	+0.58*	−0.13
Water-soluble P	−0.002	+0.76**	+0.64**	+0.08

*Significant at 5% level **Significant at 1% level.

TABLE 6—CORRELATION COEFFICIENT BETWEEN VARIOUS FORMS OF INORGANIC PHOSPHATE AND AVAILABLE P_2O_5 IN WATER-LOGGED SOILS, ppm

Available P_2O_5	Saloid-bound P Water-logging period (days)			Al-P Water-logging period (days)			Fe-P Water-logging period (days)			Ca-P Water-logging period (days)		
	7	30	60	7	30	60	7	30	60	7	30	60
Olsen P	+0.05	+0.60*	+0.09	+0.89**	+0.91**	+0.78**	+0.88**	+0.88**	+0.95**	+0.09	+0.08	+0.07
Bray's 1-P	−0.01	+0.32	−0.14	+0.92**	+0.49	+0.46	+0.63*	+0.72**	+0.06	−0.02	−0.05	−0.05
Water-soluble P	+0.52*	+0.55*	+0.42	+0.63*	+0.65**	+0.75**	+0.54*	+0.61*	+0.69**	+0.50	+0.53*	+0.51*

*Significant at 5% level **Significant at 1% level

form in water-logged soils. However, under waterlogged condition calcium-phosphate did not show any significant correlation with phosphorus determined by Olsen's method which indicates that only a small fraction of calcium-phosphate constitute to the available phosphorus content in the water-logged soils.

Acknowledgement

Thanks are due to Dr. D. L. Deb, Soil Scientist, for his help and interest in this study.

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[Original mss. received on Oct. 15, 1971]

UDC 635.64: 632.95: 546.46

Rhizosphere and rhizoplane mycoflora of healthy and virus-infected plants of *Lycopersicum esculentum* in relation to treatment with different concentrations of magnesium as magnesium chloride has been studied. 125 ppm. concentration of magnesium proved best for the growth of the plant, virus concentration, amino acid content of root and fungal population both in healthy and diseased sets. The effect of magnesium was more pronounced on rhizosphere population than rhizoplane.

Investigations into Rhizosphere Mycoflora
Part 10—Mycoflora of Healthy and Virus-infected *Lycopersicum Esculentum* in Relation to Magnesium Treatment

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Amongst the various factors which determine the rhizosphere microbial complex of species, plant condition and root exudation are the important variables. The supply of nutrients to the plant affects the plant growth which, in turn, is expected to regulate the root-leakage both in type and amount. Rovira[1], while discussing in detail about plant root exudate, observed that little work has been done on the influence of nutrient levels on the exudation of organic compounds by plant roots[1]. Only two studies, viz. those of Bowen[2] and Rovira[3], have been reported by the latter. A marked effect of plant nutrition and exudation of amino acids by roots was observed by Bowen[2]. However, no significant difference in the exudation of amino acids from roots of tomato, subterranean clover and phalaris grass over four calcium levels was obtained by Rovira[1]. With this viewpoint it was proposed to investigate the effect of certain trace elements on the rhizosphere mycoflora. The present work deals with the effect of magnesium on the rhizosphere and rhizoplane mycoflora of *Lycopersicum esculentum* Mill var. Best of all. The effect of magnesium has been studied on rhizosphere population of healthy and virus (PVX) infected plant of *L. esculentum.*

Materials and Methods

Lycopersicum esculentum Mill var. Best of all was selected for the present study. The plants were raised in sand culture as described by Hewitt[4] and Ellis and Swaney[5]. Nutrient solution containing various concentrations, viz. 50, 125, 250 and 500 ppm of magnesium ($Mg\,Cl_2$), was prepared using the procedure of Mclean and Cook[6]. 1 ml. concentrated solution of the micronutrient elements was added to 1 lit. of nutrient solution[7], maintaining the pH at 7 just before use.

To get the virus-infected plants' potato virus X (PVX), maintained on *Nicotiana tobacum* var., White Burley in insect-proof chamber was inoculated as described by Singh[8].

20 replicates were maintained for different healthy (H) and virus-infected (D) sets in case of each magnesium level. 100 ml. of the nutrient solution was irrigated to each plant at one week's interval and control set (CU) was supplied with equal amount of distilled water. The plants were irrigated with distilled water, whenever necessary.

The rhizosphere (RS) and rhizoplane (RP) fungal population was assessed by the methods described by Mishra[9]. The population was calculated on the basis of dry weight of the root in rhizosphere sets. In rhizoplane region infection percentage of inoculated root-fragments was also counted.

The fresh and dry weight of the shoot and the length of the shoot was determined at the 60th day of inoculation of the virus. The virus concentration was described as average local lesions produced on 20 leaves of *Chenopodium amaranticolor* Coste and Reyn.

The amino acid contents of the root of each set was determined chromatographically by the method suggested by Smith[10]. Chlorophyll concentration of leaf was assessed by the procedures followed by Peach and Tracey[11]. The data in case of amino acid and chlorophyll concentration were expressed as g./2 g. of fresh weight of root and leaf respectively.

Results

36 fungal isolates were cultured from rhizosphere and rhizoplane regions of all the 4 treatments of magnesium and control set. 4 species of *Phycomycetes*, 1 of *Ascomycetes*, 20 of *Deuteromycetes* and 1 of *Mycelia Sterilia* were isolated. *Aspergillus* alone was represented by 10 species (including ascogenous species). 25 and 17 fungal species were isolated from rhizosphere and rhizoplane regions respectively in the present study (Table 1).

Seven, 8, 12, 6 and 7 species from healthy plants and 8, 9, 22, 9 and 10 species from diseased plants were recorded from CU, 50, 125, 250 and 500 ppm. magnesium concentrations respectively in rhizosphere region, whereas at corresponding concentrations 6, 5, 7, 3 and 6 species from healthy sets and 9, 10, 7, 6 and 8 species from diseased sets, were cultured from rhizoplane regions respectively (Table 1).

Rhizopus nigricans and *Cladosporium epiphyllum* were obtained from all the concentrations of magnesium in both H and D sets in rhizosphere zone, whereas in rhizoplane zone *Aspergillus ustus* and *Fusarium oxysporum* were present throughout at all the concentrations in both H and D plants (Table 1). *Phoma humicola*, *Aspergillus ochraceus*, *A. tamarii*, *Myrothecium roridum*

TABLE 1—DISTRIBUTION OF FUNGI IN THE RHIZOSPHERE AND RHIZOPLANE REGIONS OF HEALTHY AND VIRUS-INFECTED *Lycopersicum esculentum* IN RELATION TO MAGNESIUM TREATMENT

Fungal Species	Magnesium Concentration, ppm									
	Cu		50		125		250		500	
	H	D	H	D	H	D	H	D	H	D
Rhizopus nigricans	+	++	++	+/+	+/+	+/+	++	+/+	+	+/+
Mucor racemosus		+	+	+						
M. hiemalis	++	−/+	−/+	−/+	+/+	+/+	+	+	+/+	+/+
M. heterogamous	+	+				+			+	+
Aspergillus nidulans								+		+
Phoma humicola		−/+				+				
Trichoderma viride	+	+	+	++/+	+	+	+	+	−/+	+
Aspergillus fumigatus	+		+		+	+		+	+	
A. flavus		−/+		+/+	+/+	+/+			−/+	
A. terreus	+		+/+	+/+	+	+	−/+	−/+	+	+/+
A. ochraceus						+				
A. flavipes					+	+				
A. ustus	−/+	−/++	−/++	−/++	+/++	+/+	−/++	+/++	++/++	++/++
A. tamarii						+				
A. aculeatus			+		+	+				−/+
A. niger	−/+	+/+		+	+	+	+			−/+
Penicillium chrysogenum		+	−/+	+/+		+		+		+
Penicillium sp. 1			+	+	+	+				
Cladosporium epiphyllum	+	+/+	+	+	++/+	+/+	+	++	+	+
C. herbarum	−/++					+				+
Humicola fuscoatra						+	+			
Curvularia lunata	−/+	+/+				+				
Alternaria tenuis				−/+				−/+		
Fusarium oxysporum	−/+	−/+	−/+	−/+	−/+	+/++	−/+	−/+	−/+	−/+
Myrothecium roridum						++/+				
White sterile fungus	−/+	−/+		−/+	−/+			+/+	−/+	−/+
Total No. of Fungi	7/7	8/9	8/5	9/10	12/7	22/7	6/3	9/6	7/6	10/8

++ indicates dominantly present; + present; − absent; Numerator rhizosphere data; Denominator rhizoplane data.

and *Fusarium oxysporum* (125D), and white sterile fungus (250D) were of specific distribution in rhizosphere region of the sets listed in the brackets. In rhizoplane region specific fungi were *Phoma humicola*, *Cladosporium herbarum* (OUD), *Aspergillus aculeatus* (500D), *Myrothecium roridum* (125D).

In RS region, *Rhizopus nigricans* (CUD, 50H, 250H), *Mucor-hiemalis* (CUH), *Trichoderma viride* (50D), *Aspergillus ustus* (500-H & D), *Cladosporium epiphyllum* (125H, 250D) and *Myrothecium roridum* (125D) were dominant species, whereas *Aspergillus ustus* (CUD, 50-H & D, 125H, 250-H & D and 500-H & D), *Cladosporium herbarum* (CUH) and *Fusarium oxysporum* (125D) were observed to be dominant in RP region indicated in the brackets (Table 1). The rest of the isolates were distributed in various sets. The maximum number of fungal species was recorded in 125 ppm. set in both H and D plants in rhizosphere region, whereas these values for rhizoplane region were exhibited by 10 (50D) and 7 (125H) respectively from the sets indicated in the brackets. The number of fungal species in RS regions of D plants was always higher than that of H plants. The pattern in the distribution of number of species in RP region in D and H plant was similar to RS region (Table 1).

The trend of variation in fungal population of healthy plant of RS region exhibited a regular pattern. The increase in magnesium level resulted in an increase in the population and it reached the highest at 125 ppm and thereafter a gradual decrease was observed. In the diseased plant also a similar trend was observed. The infection percentage recorded in the case of RP region was the maximum in 50 and 500 ppm sets both in D and H sets. The percentage was comparatively low in 125 and 250 sets of both D and H plants. In the control set also, the percentage infection was high (Table 2).

The virus concentration, determined as average local lesions produced on 20 leaves of *Chenopodium amaranticolor*, was 9, 27, 32, 20 and 10 ($\times 10$) in control untreated, 50, 125, 250 and 500 ppm sets respectively (Table 3). The fresh and dry weight of shoot of *Lycopersicum esculentum* was of the maximum value at 125 ppm magnesium level in both H and D plants. The chlorophyll concentration of leaf was also the maximum at 125 ppm concentration of magnesium (Table 3).

TABLE 2—RHIZOSPHERE FUNGAL POPULATION ($\times 10^4$), INFECTION PERCENTAGE AND VIRUS CONCENTRATION OF HEALTHY AND DISEASED *Lycopersicum esculentum* WHEN TREATED WITH DIFFERENT CONCENTRATIONS OF MAGNESIUM CHLORIDE

Magnesium Concentration, ppm	Fungal Population ($\times 10^4$)	Infection % of RP Region	Virus Concentration
Control (Cu)			
H	2.25	100	—
D	1.60	100	90
50			
H	4.23	100	—
D	2.00	100	270
125			
H	8.60	90	—
D	2.90	80	310
250			
H	1.8	90	—
D	2.10	70	200
500			
H	1.55	100	—
D	1.90	90	100

H = Healthy
D = Diseased

TABLE 3—EFFECT OF MAGNESIUM NUTRITION ON GROWTH OF *Lycopersicum esculentum*

Magnesium Concentration, ppm	Chlorophyll 'a'	Chlorophyll 'b'	Fresh Weight of Shoot, g.	Dry Weight of Shoot, g.	Shoot Length, cm.
Control (Cu)					
H	3.0	3.5	6.0	0.7	20
D	2.0	2.0	3.0	0.3	15.0
50					
H	5.5	3.5	12.0	1.1	30.0
D	3.0	3.0	4.0	0.35	18.0
125					
H	6.0	4.0	12.5	1.2	33.0
D	4.0	4.0	6.0	0.5	23.0
250					
H	6.0	3.0	10.0	0.8	23.0
D	4.0	4.0	5.0	0.45	20.0
500					
H	6.0	4.0	8.0	0.7	21.0
D	2.0	3.0	4.0	0.4	11.0

H = Healthy
D = Virus-infected

14 amino acids were chromatogrammed from the root of H and D plants of different treatments of magnesium concentration. Threonine, Tryptophane and unidentified acid (Rf. 0.65) were detected from all the treatments. Except glutamic acid which was obtained only from the D set, other acids were of common occurrence in D and H sets. The number of amino acids in RS of H plants from CU to 500 ppm magnesium levels was 9, 9, 10, 10 and 9 respectively, whereas the number at the corresponding magnesium levels in D plant was 8, 10, 11, 9 and 9 accordingly. The total amount of recognized amino acids

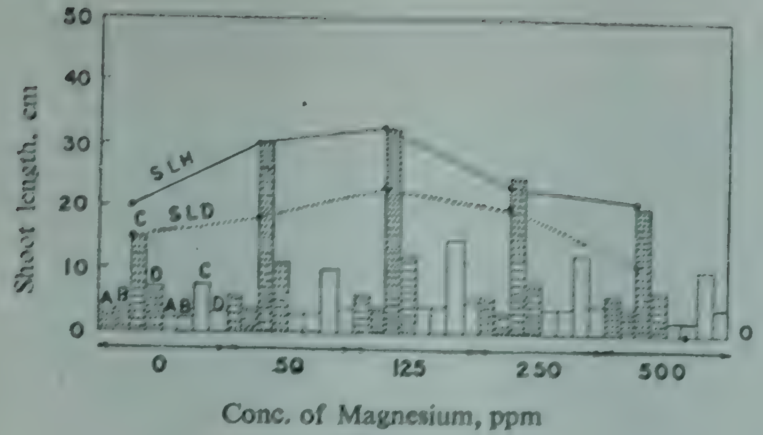

Fig. 1

A—Chlorophyll 'a' B—Chlorophyll 'b'

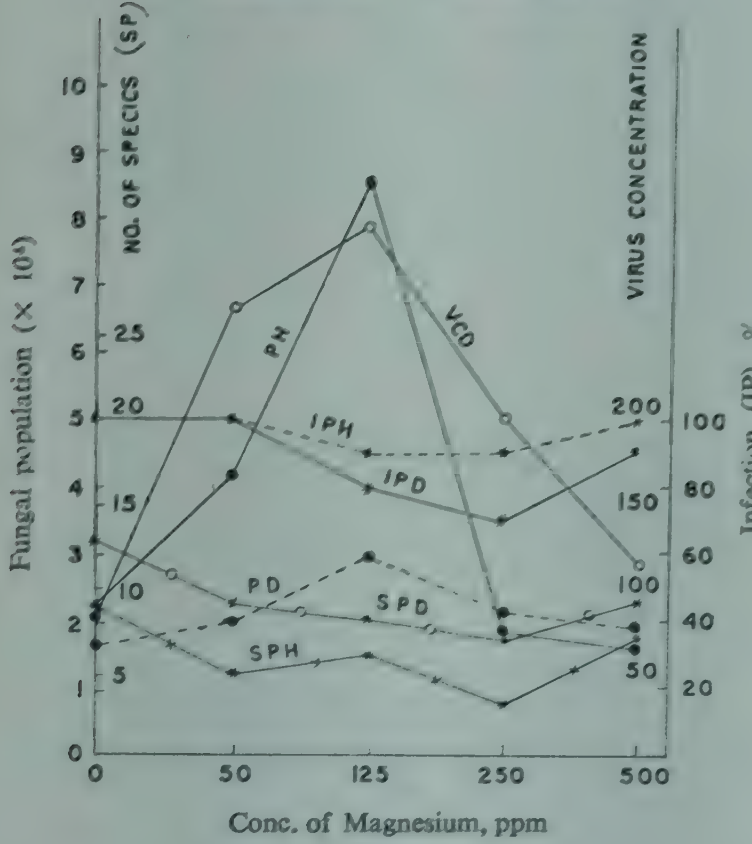

Fig. 2

expressed at μg./2 g. of fresh root, was found to be always higher in the diseased sets than in the healthy one. The magnesium supply increased the amino acid content of roots both in H and D sets. The increase was more pronounced in the amount of the acids (Table 4).

125 ppm concentration of magnesium proved better for the development of plant growth and fungal population as well. The number of fungal species, fungal population, amino acid content of root, all were higher at this concentration in the present study.

Discussion

Increase in rhizosphere mycoflora with magnesium supply was apparent from the results of the present study. The trend of variation in rhizosphere population in both the sets, i.e. healthy and diseased, was nearly alike. 125 ppm was most favourable both for H and D sets in respect to plant growth, chlorophyll content and rhizosphere population. Increase in amino acids of roots was also observed simultaneously up to 125 ppm magnesium level. The rhizosphere fungal flora is affected considerably with the plant condition and the physio-chemical characteristics of the soil and the population has been reported to be the maximum when the plant growth is the most luxuriant. The root exudation, which primarily affects the rhizosphere population in the earlier stages, is also mostly maximum when the plant growth is the best[16-18].

Photosynthetic activity of the plant has been observed to affect the root exudation and consequently the rhizosphere population. Defoliation of the plant to a varying degree caused variation in root exudation, and the rhizosphere population was the maximum in the plants where the upper young leaves were left intact[18]. Magnesium, an important constituent of plant materials, is needed in various ways for the metabolic pool. In the present study, the effect of the mineral (Mg.) on the rhizosphere population may either be direct by stimulating the growth of the fungal population in the soil or indirect through plant by changing its physiological condition. The maximum plant growth, chlorophyll content and amino acid content of the root in the set, supplied with 125 ppm magnesium resulted to favour the highest fungal population. The effect of magnesium thus seems to be more of an indirect type through the plant, the possibility, however, through the soil may also not be altogether overruled. The increase in root exudation by nutrient supply has also been reported by Bowen[2].

The effect of magnesium supply with respect to rhizosphere fungal population was nearly alike in both H and D sets. Surprisingly enough, the maxima in rhizosphere population and virus concentration were at the same point, i.e. in 125 ppm set. The rhizosphere population, however, was always low in diseased set as compared to corresponding healthy set. Variation in rhizosphere population of healthy and virus-infected plants has been reported by Mishra *et al*[20,21]. The population has always been observed to be higher in rhizosphere of healthy plants. Higher root exudation was supposed to be the reason for increased population in healthy plants by these workers. In the present study, however, the condition is different and the amount of amino acids in the roots of the diseased plants is always greater but the rhizosphere population is low (Tables 2 and 3). The magnesium supply, the variation in the nature of the host plant and virus may possibly be the reasons for this deviation.

TABLE 4—REPRESENTATION OF AMINO ACIDS IN THE ROOT OF *Lycopersicum Esculentum* IN RELATION TO MAGNESIUM TREATMENT

Amino Acids	Magnesium Concentration, ppm									
	Cu		50		125		250		500	
	H	D	H	D	H	D	H	D	H	D
Alanine	750	425	—	385	—	675	430	835	125	325
Cystein	—	—	1650	2230	1130	—	1350	600	130	250
Glutamic Acid	—	350	—	—	163	285	163	285	—	170
Glycine	75	—	—	—	175	1600	—	—	—	—
Iso-leucine	225	—	—	88	—	290	—	—	182	—
Leucine	355	137	175	200	250	—	145	650	280	225
Methionine	—	292	—	180	70	190	—	211	136	275
Proline	87	75	140	125	180	750	200	—	—	80
Serine	—	—	80	50	190	525	125	—	85	—
Threonine	175	390	180	220	50	250	50	195	140	250
Tryptophane	80	370	170	175	130	650	75	150	125	180
Unidentified 1 (Rf 0.60)	+	—	+	—	+	+	—	+	—	—
Unidentified 2 (0.65)	+	+	+	+	+	+	+	+	+	+
Unidentified 3 (Rf. 0.55)	—	—	+	—	—	+	+	—	—	—
Total amount of identified acids	1717	2039	2395	3653	2675	4930	2538	2926	1204	1755
No. of Amino Acids	9	8	9	10	10	11	10	9	9	9

In the rhizoplane region, the trend of variation, though almost of similar type as in H and D sets, is different from the rhizosphere region. The maximum population was at 50 and 500 ppm. which was equal to the control set. Rhizoplane population does not seem to be affected appreciably by the magnesium supply in the experimental condition prevailing in the present study.

Acknowledgements

The authors are thankful to Prof. K. S. Bhargava, Head, Department of Botany, University of Gorakhpur, Gorakhpur, U. P., for providing the necessary laboratory and library facilities.

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[Original mss. received on Sept. 14, 1972]

UDC 631.4: 6.31.811.2: 632.12

The addition of four different ammonium salts, viz. ammonium nitrate, ammonium chloride and ammonium sulphate, and urea with 0.2, 0.4 and 1.0 per cent concentrations was found to increase phosphate fixation by some typical Indian soils under three different moisture treatments—high, moderate and low moisture conditions—at 30°C after one month's time of reaction. It has been observed that generally maximum phosphate fixation by alluvial soil is obtained with treatment having more initial soil moisture in presence of 1.0 per cent ammonium nitrate at 30°C. This is followed by ammonium sulphate and urea additions in the red and alkali soil samples. Generally, the soils having loamy sand or sandy loam texture have been observed to affect much their phosphate fixation capacity in presence of different ammonium salts at 30°C. The minimum phosphate fixation was generally found with red and laterite soils with 1.0 per cent of the applied ammonium salts especially with ammonium chloride and with treatment having low initial soil moisture.

Fixation of P_2O_5 by Soils in Aqueous Media in Presence of Ammonium Salts and Urea

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Introduction

The review[1] on phosphate fixation by Indian soils and clay minerals shows that studies on the effect of ammonium salts on the extent of phosphate fixation by Indian soils in aqueous media are lacking. However, the effect of ammonium salts on phosphate fixation by certain Indian clay minerals has been studied by many workers[2–5], who found that in presence of ammonium chloride, montmorillonite gave the maximum intake of phosphate. In this paper, phosphate fixation by five typical Indian soils in presence of four different ammonium salts at 1.0 per cent concentration under three moisture conditions (treatments A, B and C) has been studied and discussed.

Experimental

Five typical Indian soils, viz. black cotton (Krishna Dist., A.P.), laterite (Coimbatore, Tamil Nadu), alluvial (Naini, Allahabad), red (Ranchi, Bihar) and alkali (Soraon, Allahabad) were collected from a depth 0-15 cm. The samples were dried, pulverized, finally passed through 100 mesh (BSS) and then analysed for their different physico-chemical properties (Table 1) by the reported methods.[6] For observing the effect of different ammonium salts on phosphate fixation, the following three moisture treatments were given to each sample.

Treatment A: 10 g. of each sample was taken in glass dishes and treated with four different ammonium salts, viz. ammonium chloride, ammonium nitrate and ammonium sulphate, and urea of 0.2, 0.4 and 1.0 per cent concentration. The samples were further treated with sufficient and measured amount (15 ml.) of water to the above saturation point and allowed to react in that condition for a month.

Treatment B: 10 g. of each sample was taken in glass dishes and treated with the same concentrations of the ammonium salts and urea used in treatment A. Sufficient water (10 ml.) was added to submerge the sample and allowed to remain in that condition for a month.

Treatment C: 10 g. of each sample was taken and then treated with the same ammonium salts and urea in concentrations as mentioned in treatments A and B. To this, 5 ml. of water was added periodically to keep it just moist and allowed to stand for a month for reaction.

After a month the soils were dried and pulverized in an agate mortar and kept in oil paper bag.

TABLE 1—ANALYSIS OF SOILS

[0-15 cm.]

Constituents	Soils				
	Black Cotton, %	Laterite, %	Alluvial %	Red, %	Alkali, %
HCl Insoluble	66.18	84.75	86.68	72.33	86.97
Total R_2O_3	21.83	9.47	8.58	16.95	7.15
,, Fe_2O_3	9.44	4.08	3.48	6.56	2.60
,, Al_2O_3	12.15	5.32	4.90	10.32	4.46
,, CaO	1.61	0.46	0.26	0.50	0.63
,, P_2O_5	0.24	0.07	0.20	0.08	0.09
,, Na_2O	0.48	0.53	0.45	0.35	1.12
,, Organic carbon	0. 5	0.77	0.54	0.88	0.32
,, N	0.05	0.06	0.08	0.06	0.05
C/N ratio	19.00	11.17	6.75	14.37	6.40
	EXCHANGE PROPERTIES, m.e./100 g. SOIL				
Total C.E.C.	32.17	49.56	16.95	23.47	13.48
,, Ex. cation	29.66	33.33	13.26	16.42	9.10
,, Ex. Na^+	0.52	1.65	0.63	0.03	7.30
Texture	Clay	Sandy Loam	Loamy Sand	Sandy Clay Loam	Sandy Loam
pH	7.50	8.10	7.50	5.30	10.40

5 g. of the treated soil (treatments A, B and C) was taken in a 100 ml. volumetric flask and a required volume of 50 mg. P_2O_5 in the form of phosphoric acid (H_3PO_4) was added to it. The volume in each case was made up to 100 ml., the contents were then mixed and allowed to stand for 24 hours. Next day, 5 ml. of the supernatant liquid was taken and analysed for P_2O_5 colorimetrically[7,8] using 660 mμ red filter.

The pH values were measured[9] by Leeds and Northrup pH meter operated on 220V and 50 cycles AC mains. The initial values were taken just after the addition of ammonium salts whereas the final pH values were taken after the incubation period.

The difference in concentration between the P_2O_5 added to the fixation system and the P_2O_5 present in the system after completion of the experiment was taken as the amount of P_2O_5 fixed by soils at different conditions.

Results and Discussion

A perusal of Tables 2 to 5 will show that in almost all cases, phosphate fixation by five Indian soils increases in presence of all the ammonium salts at 30°C. but its extent

TABLE 2—FIXATION OF P_2O_5 BY SOILS IN AQUEOUS MEDIUM IN PRESENCE OF AMMONIUM NITRATE AT 30°C

mg. P_2O_5 added/5 g. Soil = 50 mg.

Soil	mg. P_2O_5 Fixed/5 g. Soil			Initial pH			Final pH		
	Treatment			Treatment			Treatment		
	A	B	C	A	B	C	A	B	C
1	6.0	6.0	4.0	5.6	6.6	6.6	6.0	6.9	7.0
2	14.0	2.0	−7.0	4.8	6.0	5.8	6.2	6.3	5.7
3	24.0	−1.0	2.0	5.0	5.2	5.1	5.5	5.2	5.6
4	8.0	−9.0	5.0	4.6	4.8	5.2	5.0	4.8	5.9
5	3.0	−5.0	18.0	6.0	7.0	7.0	6.0	6.9	7.7

varied with the type of the soil, kind of treatment of the soil (treatments A, B and C) and also with the addition of the different ammonium compounds.

The detailed data on the fixation of P_2O_5 by soils in presence of different concentrations of ammonium salts or urea have been avoided but Tables 2 to 5 are sufficient to indicate the maximum fixation at 1.0 per cent concentration.

From Tables 2 to 5, it may be observed that the maximum phosphate fixation has been obtained by alluvial soil (soil 3), under treatment A with the addition of ammonium nitrate and at 30°C. The efficiency order of the ammonium salts and urea regarding the maximum fixation of P_2O_5 by all the soils under all the treatments (treatments A, B, and C) has been found to lie in the following decreasing order: ammonium nitrate>ammonium sulphate>urea >ammonium chloride.

This order of efficiency is found in case of each of the

TABLE 3—FIXATION OF P_2O_5 BY SOILS IN AQUEOUS MEDIUM IN PRESENCE OF AMMONIUM CHLORIDE AT 30°C

mg. P_2O_5 added/5 g. Soil = 50 mg.

Soil	mg. P_2O_5 fixed/5 g. Soil			Initial pH			Final pH		
	Treatment			Treatment			Treatment		
	A	B	C	A	B	C	A	B	C
1	14.0	1.0	2.0	5.6	6.6	6.6	6.2	6.7	6.7
2	14.0	9.0	3.0	4.8	6.0	5.8	6.0	6.1	6.0
3	2.0	8.0	−6.0	5.0	5.2	5.1	5.0	5.7	4.8
4	7.0	1.0	2.0	4.6	4.8	5.2	5.3	5.9	5.3
5	2.0	2.0	10.0	6.0	7.0	7.0	6.2	7.1	7.3

TABLE 4—FIXATION OF P_2O_5 BY SOILS IN AQUEOUS MEDIUM IN PRESENCE OF AMMONIUM SULPHATE AT 30°C

mg. of P_2O_5 added/5 g. Soil = 50 gm.

Soil	mg. P_2O_5 Fixed/5 g. Soil			Initial pH			Final pH		
	Treatment			Treatment			Treatment		
	A	B	C	A	B	C	A	B	C
1	12.0	22.0	−1.0	5.6	6.6	6.6	6.3	7.1	6.6
2	14.0	22.0	−5.0	4.8	6.0	5.8	6.3	6.2	5.6
3	23.0	18.0	4.0	5.0	5.2	5.1	6.2	5.6	5.3
4	4.0	2.0	−3.0	4.6	4.8	5.2	4.7	6.0	5.1
5	16.0	4.0	4.0	6.0	7.0	7.0	7.2	7.1	7.2

TABLE 5—FIXATION OF P_2O_5 BY SOILS IN AQUEOUS MEDIUM IN PRESENCE OF UREA AT 30°C

mg. of P_2O_5 added/5 g. Soil = 50 mg.

Soil	mg. P_2O_5 Fixed/5 g. Soil			Initial pH			Final pH		
	Treatment			Treatment			Treatment		
	A	B	C	A	B	C	A	B	C
1	10.0	11.0	13.0	5.6	6.6	6.6	6.6	6.9	7.0
2	8.0	13.0	5.0	4.8	6.0	5.8	5.4	6.3	6.1
3	20.0	15.0	13.0	5.0	5.2	5.1	5.6	5.7	5.4
4	16.0	0.0	7.0	4.6	4.8	5.2	6.2	4.8	5.0
5	22.0	17.0	17.0	6.0	7.0	7.0	7.6	7.5	7.4

treatments also but maintaining the same order, the extent of phosphate fixation in presence of the ammonium salts and urea increased according to the treatments as: Treatment A>Treatment B>Treatment C. It is evident from the above orders that the soils under treatment A (more initial soil moisture) which gives the maximum phosphate fixation in presence of ammonium salts and urea is due to the fact that the soils having low moisture (treatment C) will have slow movement of phosphate ions and the latter will fix comparatively less amount of phosphate (Tables 2 to 5). This will also be true in relation to phosphate availability. The foregoing results show that the application of different types of ammonium salts should be made according to the type of soil, nature of moisture treatments given to the soils and also concentration of the applied ammonium salts (here 1.0 per cent).

It may again be observed that when phosphate application is along with the ammonium salts (Treatment A), alluvial soil of loamy sand texture records the maximum fixation of P_2O_5 whereas the red (sandy clay loam) and laterite (sandy loam) soils give the minimum phosphate fixation at 30°C irrespective of the nature of ammonium salts and urea added. This shows that the effect of ammonium salts towards increasing phosphate fixation will generally be more prominent with the loamy sand (alluvial) and sandy loam (alkali) soils, i.e. in soils of low capillarity or high porosity (Tables 1 to 5). Further, it has been observed that lowering of pH with the addition of different ammonium salts under different moisture treatments (A, B and C) gave generally the maximum phosphate fixation by all the five soils (Tables 2 to 4).

De and Sharma[2] gave the following mechanism of phosphate fixation by some Indian montmorillonites in presence of different ammonium salts:

$$H_3PO_4+NH_4Cl \longrightarrow NH_4H_2PO_4+HCl \qquad \text{(i)}$$

$$H_3PO_4+NH_4NO_3 \longrightarrow NH_4H_2PO_4+HNO_3 \qquad \text{(ii)}$$

$$H_3PO_4+(NH_4)_2SO_4 \longrightarrow (NH_4)_2HPO_4+H_2SO_4 \qquad \text{(iii)}$$

According to them, the $H_2PO_4^-$ and HPO_4^{2-} ions are more easily removed from the solution by the clay minerals than phosphoric acid and there would thus be comparatively lesser quantity of hydrogen ions present in the liquid phase inducing an increase in the resultant pH. Further, they pointed out that in presence of ammonium salts, the ratio of $H_2PO_4^-/HPO_4^{2-}$ (H/H) might have also contributed to the phenomenon of phosphate adsorption by clay minerals. The value of H/H would decrease with the decrease of soil pH by the addition of ammonium salts and thus affect the phosphate fixation[10,11].

The explanation may also be true in the present system as it has been observed that with the fixation there is always an increase in the resultant pH indicating release of OH^- ions consequent on the fixation of $H_2PO_4^-$ formed due to the interaction of ammonium salts and phosphoric acid. It is obvious that as the extent of the formation of $H_2PO_4^-$ ions is dependent in the present system on the soil type, soil treatment, nature and concentration of the ammonium salts and urea added, there is a difference in the measure of phosphate fixation.

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[Original mss. received on Oct. 6 1972]

UDC 547.498.8: 548.5

The crystallographic properties of melamine acetate and melamine monohydrochloride hemihydrate have been studied by x-ray diffraction. The powder diffraction data showed that both the compounds belong to orthorhombic system. The cell dimensions of melamine acetate are: a=9.9910Å; b=9.2083Å and c=6.9252Å. The space group of melamine acetate was found to be P222 D_2^1 or Pmm2 C_{2v}^1 with four molecules per unit cell. The cell dimensions of melamine monohydrochloride hemihydrate are a=9.5347Å; b=8.7374Å and c=8.0321Å. The space group of melamine monohydrochloride hemihydrate was found to be P222 D_2^1 or Pmm2 C_{2v}^1 with 4 molecules per unit cell.

Crystallographic Data for Melamine Acetate and Melamine Monohydrochloride Hemihydrate

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Melamine, a mono-acid base, forms a number of compounds when treated with different acids. With mineral and fatty acids, it gives different substitution products. Since melamine and its substitution products are important starting materials for different industrial products, an idea of their physical parameters may be helpful in regard to their use. So far, only the infrared spectral data of melamine hydrochloride have been reported[1] with respect to its structural characteristics but no crystallographic data are known. Similarly, for melamine acetate crystallographic and other data are also not available. As a part of a research programme, a study of the crystallographic properties of melamine monohydrochloride hemihydrate and melamine acetate has been undertaken.

Preparation of the Samples

(i) *Melamine Hydrochloride Hemihydrate*: The chemicals used in the experiment were of AnalaR (BDH) quality. It is known that with hydrochloric acid (conc.), melamine forms three very stable salts, whose aqueous solution is an acid to litmus. In the present work, melamine monohydrochloride hemihydrate was prepared according to the following method: An equivalent amount of hydrochloric acid (conc.) was added to melamine saturated at 40°C and pH was adjusted to 2.0. The material was then evaporated to dryness and then kept in a desiccator for final drying. A better result is obtained if a slight excess hydrochloric acid is used.

(ii) *Melamine Acetate*: About 10 g. of melamine was taken in a beaker and 50 c.c. of glacial acetic acid was added to it. The content of the beaker was heated very gently with continuous stirring. The pH was found to be 3.5 and gelatinous precipitate appeared gradually on cooling. The precipitate was dried and kept in a desiccator for final drying.

Chemical Analysis of the Samples

Micro-analysis of the samples were done for both the compounds (Table 1).

TABLE 1

Melamine hydrochloride hemihydrate ($C_3H_7N_6Cl$, 1/2 H_2O)		Melamine acetate ($C_5H_{10}N_6O_2$)	
Observed	Calculated	Observed	Calculated
C = 22.12	C = 21.01	C = 32.12	C = 32.26
H = 4.84	H = 4.68	H = 5.32	H = 5.42
N = 48.12	N = 48.98	N = 45.82	N = 45.13
Cl = 20.34	Cl = 20.66		

X-ray Measurements

The x-ray diffraction patterns of the samples were taken in a Guinier camera in the Philips x-ray unit PW1010, using CuK$_\alpha$ radiation and the x-ray tube running at 40 KV with 20 ma. The duration of exposure was 6 hr. with each sample. The intensities of the line of the x-ray powder photographs were evaluated by visual estimation. The interplanar spacings and the corresponding Q values $Q_{hkl} = \frac{1}{d^2_{hkl}}$ of melamine acetate and melamine hydrochloride hemihydrate are listed in Tables 2 and 3. The x-ray analysis of the experimental sample indicates that the individual products are pure. Microanalysis of the samples also confirms the same. The powder pattern of both the samples were indexed by Ito's[2] method and the reciprocal cells were determined as described earlier[3].

The direct cell dimensions are as follows:

(i) *Melamine acetate*

a = 9.9901 Å

TABLE 2—FINAL AGREEMENT OF OBSERVED AND COMPUTED Q_{hkl}'S FOR MELAMINE ACETATE

Powder Diagram Line No.	dÅ	Intensity	Q (Observed)	Q (Calculated)	hkl
1.	9.9	MS	.01020	—	100
2.	9.2	W	.0118	—	010
3.	7.0	VW	.0204	—	001
4.	5.7	W	.0307	.0308	101
5.	5.05	S	.0392	.0408	200
6.	4.80	W	.0434	.0427	111
7.	4.60	VW	.0472	.0472	020
8.	4.28	M	.0545	.0518	210
9.	4.00	M	.0625	.0609	201
10.	3.82	W	.0685	.0681	021
11.	3.75	W	.0711	.0727	211
12.	3.65	VVW	.0751	.0780	121
13.	3.45	W	.0440	.0816	002
14.	3.40	W	.0865	.0873	220
15.	3.30	VS	.0918	.0918	300
16.	3.25	W	.0947	.0952	012
17.	3.16	S	.1001	.1019	310
18.	3.07	VW	.1061	.1062	030
19.	2.99	W	.1190	.1104	301
20.	2.92	VVW	.1173	.1127	311
21.	2.89	VW	.1197	.1162	130
22.	2.82	VVW	.1255	.1240	202
23.	2.79	VW	.1285	.1271	031
24.	2.62	VVW	.1457	.1462	230
25.	2.51	W	.1587	.1582	321
26.	2.44	W	.1680	.1671	231
27.	2.39	VW	.1751	.1736	302
28.	2.30	W	.1890	.1836	003
29.	2.27	VVW	.1941	.1964	330
30.	2.25	VVW	.1975	.1977	1 3
31.	2.21	VW	.2047	.2075	420
32.	2.16	VVW	.2143	.2172	331
33.	2.13	VW	.2204	.2280	140
34.	1.93	VVW	.2685	.2665	430
35.	1.90	VVW	.2747	.2722	042
36.	1.88	VVW	.2829	.2821	511
37.	1.85	VVW	.2922	.2939	033
38.	1.79	VVW	.3121	.3146	521
39.	1.73	VVW	.3341	.3339	502
40.	1.67	VVW	.3586	.3567	530
41.	1.65	VVW	.3673	.3699	441
42.	1.62	VVW	.3910	.3809	024
43.	1.601	VVW	.3001	.3934	611
44.	1.48	VVW	.4565	.4559	612

b = 9.2083 Å
c = 6.9252 Å

The crystals belong to orthorhombic system. The probable space group is P222 D_2^1 or Pmm2 C_{2v}^1. The observed density of the compound 1.440 g. cm^{-3} indicates 4 molecules per unit cell. The calculated density = 1.560g. cm^{-3}.

(ii) *Melamine monohydrochloride hemihydrate*
The direct cell dimensions are as follows:
a = 9.5347 Å

TABLE 3—FINAL AGREEMENT OF OBSERVED AND COMPUTED Q_{hkl}'S FOR MELAMINE MONOHYDROCHLORIDE HEMIHYDRATE

Line No.	dÅ	Intensity	Q (observed)	Q (Computed)	hkl
1.	9.50	M	.0110	.0110	100
2.	8.75	M	.0130	.0131	010
3.	8.00	VVW	.0156	.0155	001
4.	6.50	VW	.0237	.0241	110
5.	5.62	M	.0317	.0286	011
6.	5.20	W	.0369	.0397	111
7.	4.75	M	.0443	.0443	200
8.	4.50	W	.0494	.0544	013
9.	4.40	W	.0516	.0522	020
10	3 96	W	.0638	.0624	002
11.	3.67	VW	.0742	.0730	211
12.	3.55	VVW	.0793	.0738	102
13.	3.50	VVW	.0816	.0758	121
14.	3.45	M	.0840	.0785	012
15.	3.35	M	.0891	.0869	112
16.	3.22	S	.0964	.0961	220
17.	3.16	S	.0989	.0997	300
18.	3.10	W	.1041	.1066	202
19.	3.02	VS	.1096	.1127	310
20.	2.93	M	.1165	.1175	030
21.	2.81	M	.1266	.1218	221
22.	2.76	VVW	.1313	.1237	311
23.	2.74	VVW	.1332	.1322	031
24.	2.67	VW	.1409	.1404	003
25.	2.60	VW	.1479	.1433	131
26.	2.56	VW	.1526	.1524	103
27.	2.50	VVW	.1600	.1606	230
28.	2.45	VVW	.1666	.1672	321
29.	2.37	M	.1780	.1793	032
30.	2.35	VVW	.1811	.1854	203
31.	2.30	VW	.1890	.1917	401
32.	2.26	W	.1958	.1932	023
33.	2.20	W	.2066	.2059	411
34.	2.10	W	.2268	.2290	420
35.	2.03	W	.2427	.2388	402
36.	1.985	W	.2538	.2541	313
37.	1.970	VVW	.2577	.2579	033
38.	1.925	VVW	.2699	.2702	042
39.	1.850	VVW	.2922	.2929	323
40.	1.750	VW	.3265	.3287	520
41.	1.730	VVW	.3341	.3345	150
42.	1.710	W	.3410	.3445	521
43.	1.672	W	.3577	.3566	422
44.	1.610	M	.3858	.3863	052
45.	1.580	W	.4006	.4030	324
46.	1.408	VVM	.5046	.5008	450
47.	1.390	VVW	.5176	.5095	035
48.	1.330	VVW	.5653	.5690	405

$b = 8.7374$ Å
$c = 8.0321$ Å

The crystals belong to orthorhombic system. The probable space group is P222 D_2^1 or Pmm2 C_{2v}^1 The observed density of 1.641 g. cm^{-1} indicates 4 molecules per unit cell. Calculated density 1.704 g. cm^{-3}.

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Superintendent, Physical Research Wing, for his encouragement and interest in this work.

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[Original mss. received on Jan. 22, 1973]

UDC 547.495.9: 548.5

The crystallographic properties of guanidine dipicrylaminate have been studied by x-ray diffraction of the single crystal. The rotation and the Weissenberg photographs showed that the crystals belong to the orthorhombic system having cell dimensions: $a = 19.46$ Å, $b = 20.56$ Å and $c = 9.88$ Å. The space group of the crystal is uniquely determined to be Pbca ($D^{15}{}_{2h}$), the number of molecules per unit cell being eight.

Redetermination of Crystal Data of Guanidine Dipicrylaminate*

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Introduction

In an attempt to correlate the reaction between hexanitro-diphenylamine (dipicrylamine) and guanidine salts with structural information, complete structure analysis of guanidine dipicrylaminate ($C_{13}H_{10}N_{10}O_{12}$) has been undertaken. It was reported earlier[1] that guanidine dipicrylaminate crystallized in the monoclinic system having cell dimensions: $a = 9.141$ Å, $b = 8.868$ Å, $c = 6.766$ Å and $\beta = 107°39'$. The probable space group was reported to be P2/m with two molecules per unit cell. These results were determined from powder data by applying Ito's method[2]. The simplicity of the space group seemed to be very much encouraging, but the calculated density ($\rho_{calc} = 3.567$ gcm^{-3}) and the observed density ($\rho_{obs} = 3.606$ gcm^{-3}) indicated some doubt, because such a high density of a salt consisting only of carbon, nitrogen, oxygen and hydrogen seems to be abnormal. Hence, the observed density was first checked. The present density measurement showed a large difference from that reported earlier[1]. This prompted the authors to undertake the problem from the unit cell determination stage.

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*Presented at the 60th Session of the Indian Science Congress held at Chandigarh, during Jan. 3 to 9, 1973.

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Preparation of Single Crystals

The single crystals of the compound were grown from its saturated solution in acetone by repeated crystallization under controlled evaporation. The crystals obtained were elongated prismatic needles and deep red in colour. The melting point of the crystals was checked by scanning calorimeter and the value was 246°C, which is inconsistent with the one determined earlier[3] by the Gallenkamp melting point determination apparatus. The density (ρ_{obs}) was measured by the floation method using a mixture of bromoform and carbon tetrachloride.

X-ray Data

The axial lengths of the unit cell were determined from rotation photographs about the proposed [100]-, [010]- and [001]-axes, the third axis being the needle axis of the crystal. The axial lengths were cross-examined by the zero-level (hko, okl and hol) normal beam Weissenberg photographs. For the three dimensional data, higher layer-lines equi-inclination Weissenberg photographs were taken about c- and a-axes. All the photographs were taken in a Stoe Integrating Weissenberg camera of diameter 57.3 mm using CuK$_\alpha$ radiation. From the Weissenberg photographs, it was obvious that the crystals belong to the orthorhombic system. The volume (V) of the unit cell was determined. Number of molecules per unit cell (Z) was calculated from the observed density.

From the indices of the reflections on the Weissenberg photographs, the following conditions for possible present reflections were observed.

hkl : no condition
hko : h = 2n
okl : k = 2n
hol : l = 2n
hoo : h = 2n
oko : k = 2n
ool : l = 2n

From these conditions, the space group of the crystal was determined uniquely. The results are summarized below:

a = 19.46 Å
b = 20.56 Å
c = 9.88 Å
V = 3953 Å^3
Z = 8
ρ_{obs} = 1.700 g. cm^{-3}
ρ_{calc} = 1.673 g. cm^{-3}
Space group = Pbca (D_{2h}^{15})

Further work on the determination of the structure of the compound is in progress.

Acknowledgements

The authors are grateful to Dr. B. K. Banerjee for his interest in this work. Thanks are also due to Sri Pasupati Ghosh for supplying the pure sample.

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[Original mss. received on March 1, 1973]

UDC 521.3.015.34: 621.3.09: 621.372.54

A low-Q filter system has been described which can transform rectangular or square waves to the corresponding pure sine waves without using regenerative feedback. The effect of incorporating a triangle wave generator at the input of an ordinary band-pass filter has been pointed out. The stability of the system has been increased by using a negative feedback tuned amplifier. Results have been presented to support the conclusions made in analysing the system.

Degenerative Transformation of Low Frequency Square/Rectangular Waves to Sine Waves

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The well-known method of extracting sine waves from square or rectangular waves is to pass the latter to a frequency selective network and to consider its output as the source of the required sine waves. This type of frequency selector works faithfully for higher frequencies, viz. in the radio-frequency range and above, where the Q-value of the selective network is high but fails to do so in the audio-frequency range, particularly in the low-frequency side, because of its poor selectivity in this range of frequencies. So, unless the Q of the selective network is not high, the output of the above system will contain a large amount of harmonic distortion. But, it is difficult to raise the Q of a selective network in the low-frequency range.

The usual technique of increasing the Q-value of a selective network is to use a controlled amount of regenerative feedback in it. But, as the regeneration given to any system tends to make that system oscillatory, so a selective network with positive feedback, instead of filtering, sometimes may oscillate. Therefore, an optimization between band width of the network and its output harmonic distortion is made by controlling the positive feedback and thereby tending the system to become unstable. Such systems, while suitable for ordinary purposes, are unsuitable for control devices, such as servo amplifier, differential amplifier, low frequency phase locking of pulse generators[1], etc. In this paper a method of transforming low frequency rectangular or square waves into their corresponding pure sine waves by using an ordinary selective network without giving a regenerative feedback has been described. Here the input waves are first converted into triangular waves and then filtered in a band pass filter. However, it is to be noted from the Fourier analysis of a series of repetitive triangular waves that the ratios of amplitudes of the third and fifth harmonics to the fundamental frequency component are respectively 1:9 and 1:25 and, thus, it is evident that a triangle wave generator itself acts as a band pass filter to pass more of the fundamental component than the others. Therefore, it becomes easier to extract the fundamental component from the triangular waves by using ordinary low-Q circuits.

The block diagram of the system is shown in Fig. 1. The input square waves are first converted into triangular waves of the same frequency and then passed into a negative feedback voltage amplifier. The feedback net-

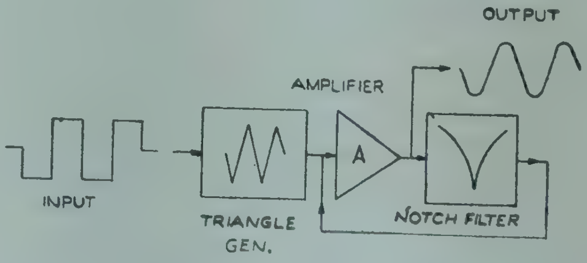

Fig. 1

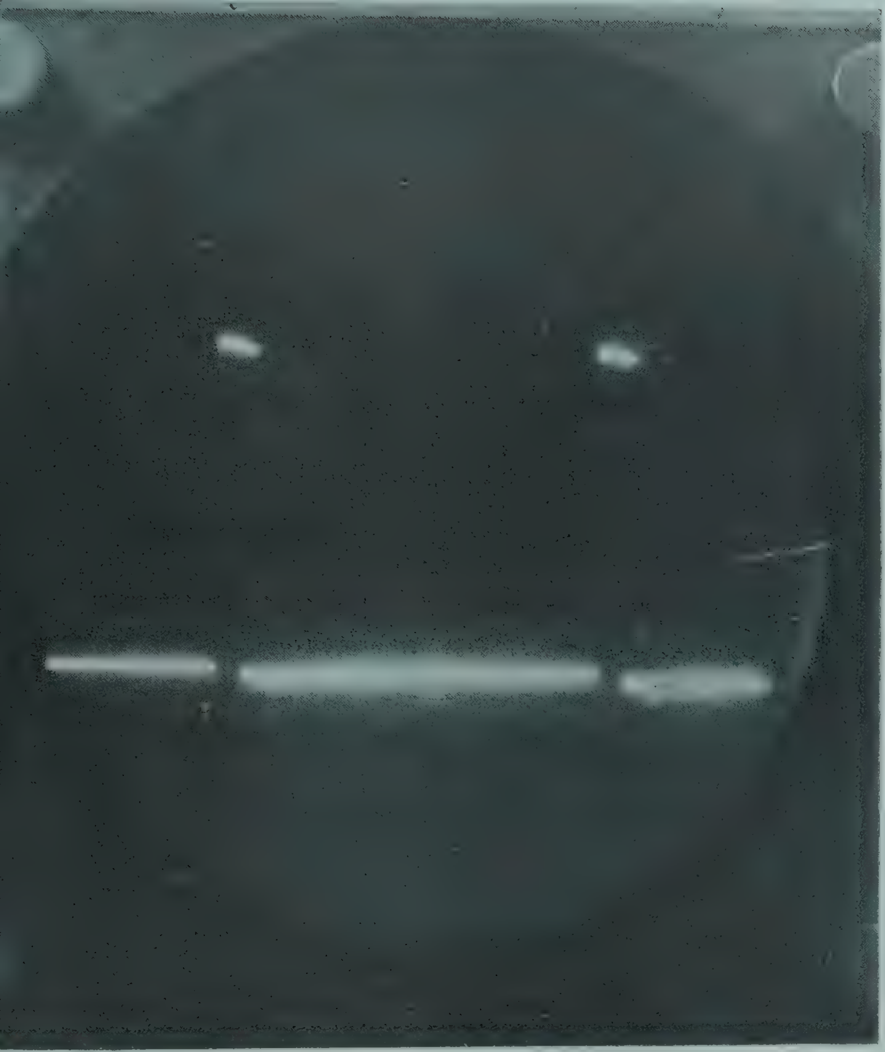

Fig. 2(a)

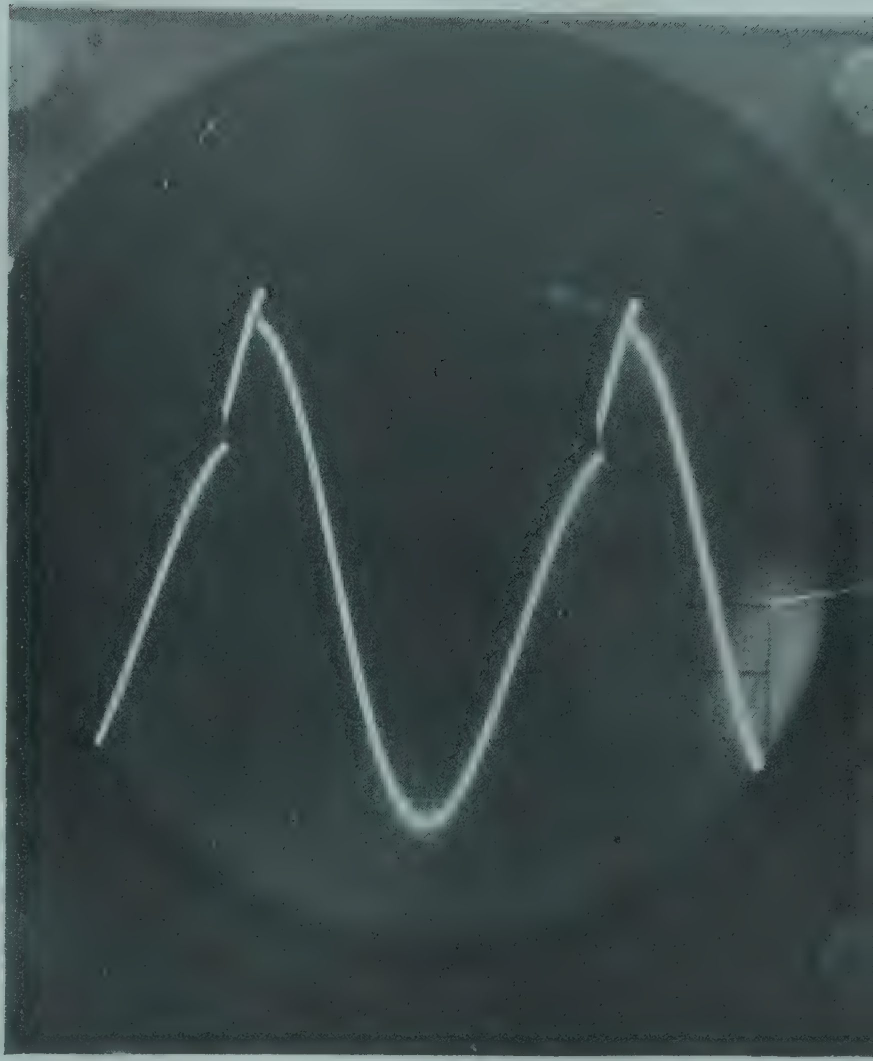

Fig. 2(b)

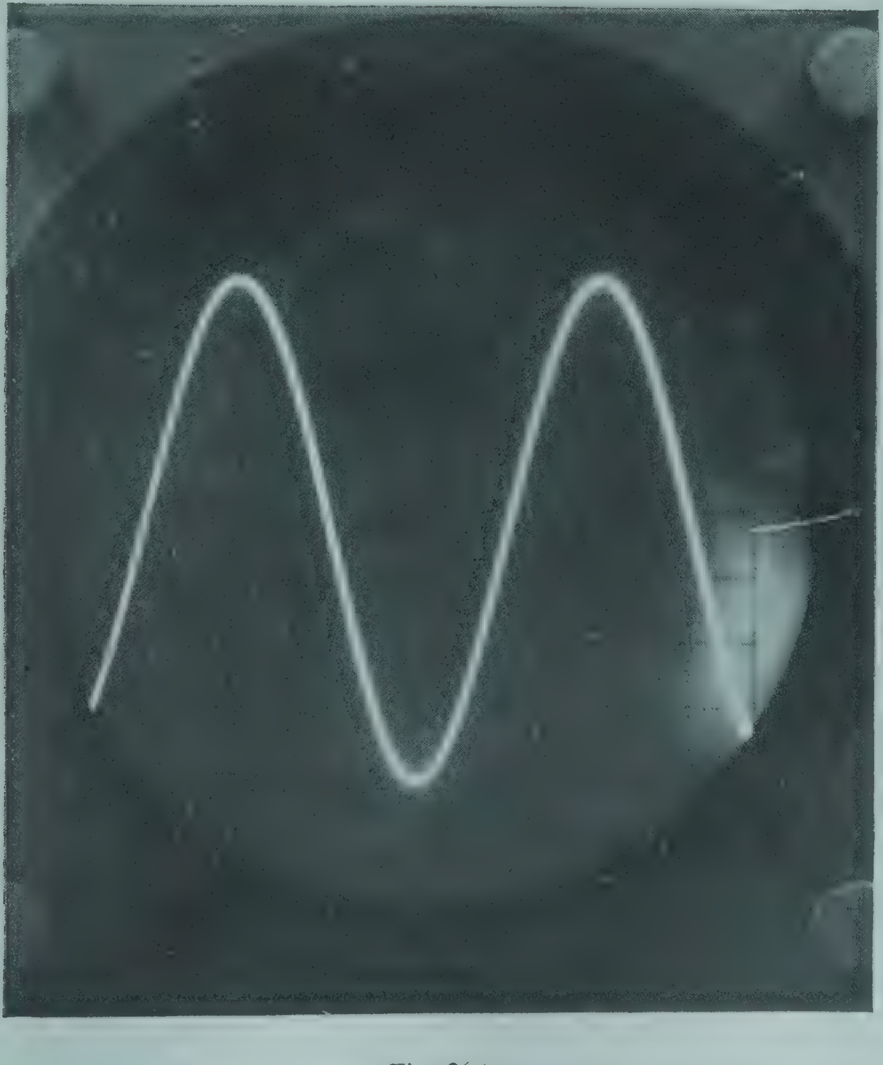

Fig. 2(c)

work of this amplifier consists of a twin-T notch filter. As the output voltage of this filter is zero at the notch frequency, the feedback is also zero at that particular frequency but sufficient negative feedback remains at other frequencies. Therefore, the gain of the amplifier is maximum at the notch frequency and falls rapidly for frequencies away from it. So, if the notch filter be tuned to the fundamental frequency component of the input wave, the output of the feedback amplifier will consist of sine waves of that frequency. As the triangle generator reduces the higher harmonics of the input wave, it is easier even for a low gain amplifier to isolate only the fundamental component.

The experiment has been carried out with rectangular waves of 25 Hz repetition frequency. A notch filter consisting of RC elements and having the notch frequency rejection of 21.6 dB as well as −3 dB band width of 310 Hz has been used. An ordinary RC coupled amplifier of gain equal to 16.5 dB and −3 dB band width of 1500 Hz has been utilized. The photographs of the output waveforms of the system comprising with and without the triangle wave generator are shown in Fig. 2. It is evident from these photographs that the output of the system incorporating the triangle wave generator consists of pure sine waves of 25 Hz frequency having no distortion. Although the above experiment has been conducted with rectangular waves of 25 Hz frequency, yet one can utilize this system for transforming square or rectangular waves of any frequency to sine waves of that frequency by simply varying the notch frequency and the time-constant of the triangle generator. It is to be noted here that the main frequency selective circuit is the negative feedback tuned amplifier and hence there is no chance of instability in the system.

Acknowledgements

The author is grateful to Dr. P. K. Ghosh of the Physical Research Wing for helpful discussions in this work. Thanks are also due to Dr. B. K. Banerjee, Superintendent, of the same wing for constant encouragement in this work.

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[Original mss. received on June 3, 1972]

TECHNOLOGY

OFFER FOR EXCHANGE

This quarterly, TECHNOLOGY, is offered in exchange with other scientific and technical journals for mutual benefit. It is already being exchanged with about eighty journals—foreign and Indian. Editors of journals devoted to all branches of science and technology and particularly fertilizer technology, applied chemistry, chemical engineering, food technology, agronomy, agricultural chemistry, soil science, fuel technology, etc. may write to the Editor of TECHNOLOGY.

UDC 661.51:06.092

In one of the fertilizer plants, the ammonia cracking unit failed after a very short run due to nitriding. The material of construction of the ammonia preheater coil was AISI 304 stainless steel and that of the cracking tube AISI 310 stainless steel. This case of failure has been studied.

Failure in an Ammonia Cracking Unit: A Case Study

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During the start-up of certain fetilizer plants, the requirements of nitrogen and hydrogen are met by the cracking of ammonia. In one fertilizer plant, failure occurred in the cracking unit only after a short run. The cracking unit consisted of two sections, viz. preheater and cracking furnace. The preheater section is situated at the top of the cracking furnace. Cold ammonia enters the preheater unit from the top and comes out from the bottom at about 350-400°C. The flue gas enters from the bottom of the cracking unit and comes out by the chimney stacks above the preheater coils. There were altogether 41 tubes in the preheater section of 20 mm. O.D. and 1.5 mm. thickness. The material of construction was AISI 304 stainless steel.

Ammonia coming out of the preheater coils enters cracking furnace tubes just below the preheater, travels downwards along the entire length of the tube and again rises up after passing through the distributor which is packed with catalyst. Finally, the gas goes out from the top of the cracking section. The material of construction of the shell and the tube was AISI 310 type of stainless steel. There were in all 16 tubes of dimension 5800 mm. long × 2.11 mm. thick and 26.7 mm. outside diameter. The shell was 5120 mm. long × 4 mm. thick and of 114 mm. outside diameter. The specified pressure condition of the tube and shell were as follows:

Tube side inlet pressure	... 1 kg./cm.^{2} gauge.
Outlet pressure from the tube	... 1000 ml. of water column.
Shell side pressure	... 30 mm. water gauge.

The specified limit of ammonia in the exit gas was 1000 ppm. at 550°C. In the furnace chamber the design temperature of the flue gas in the bottom zone is 1090°C and about 650°C at the outlet.

Failure of Preheater Coils

The preheater unit was in operation for a total period of about 1000 hours with intermittent shutdowns when leakages were first observed. The leaks were repaired but the pressure was still dropping rapidly. To check up the trouble, the entire preheater coil was opened up and altogether ten tubes were found leaking. Heavy deposition of scale was observed on the inside of the tubes.

Visual examination of the failed tubes showed that the failure had occurred due to thinning and in some cases rupture appeared to have occurred in the weld region. The failed tubes and the scales found inside the tubes were highly magnetic. A portion of the tube which was cut from outside the flue gas preheater showed magnetic pull only in the lower half of the tube circle.

Analytical checkup showed that the tube contained 18.3 per cent chromium and 8.8 per cent nickel which met manufacturers' specification. The scale scrapped from the inside of the tube was analysed as 11.7 per cent chromium, 8.4 per cent nickel and 5.5 per cent nitrogen. A hardness survey gave the following values:

Hardness of the inner surface	241 BHN
Hardness of the outer surface	156 BHN

Metallographic examination showed the structure of

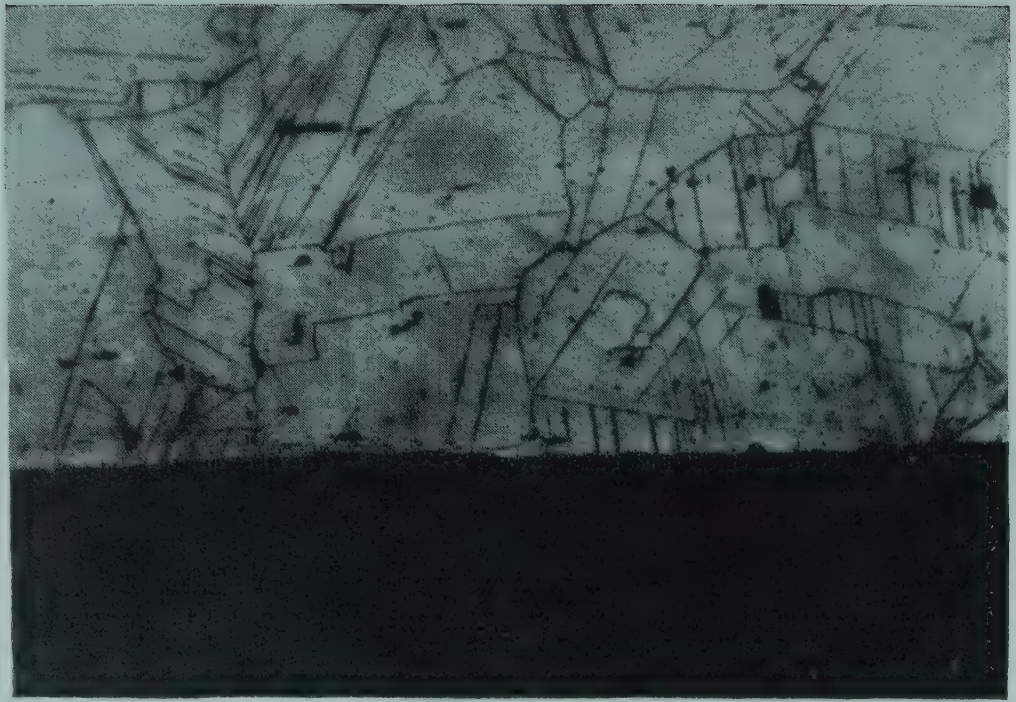

Fig. 1—Photomicrograph of the transverse section of the failed AISI 304 stainless steel ammonia preheater tube showing austenitic structure and extensive nitriding of the inner surface. × 200

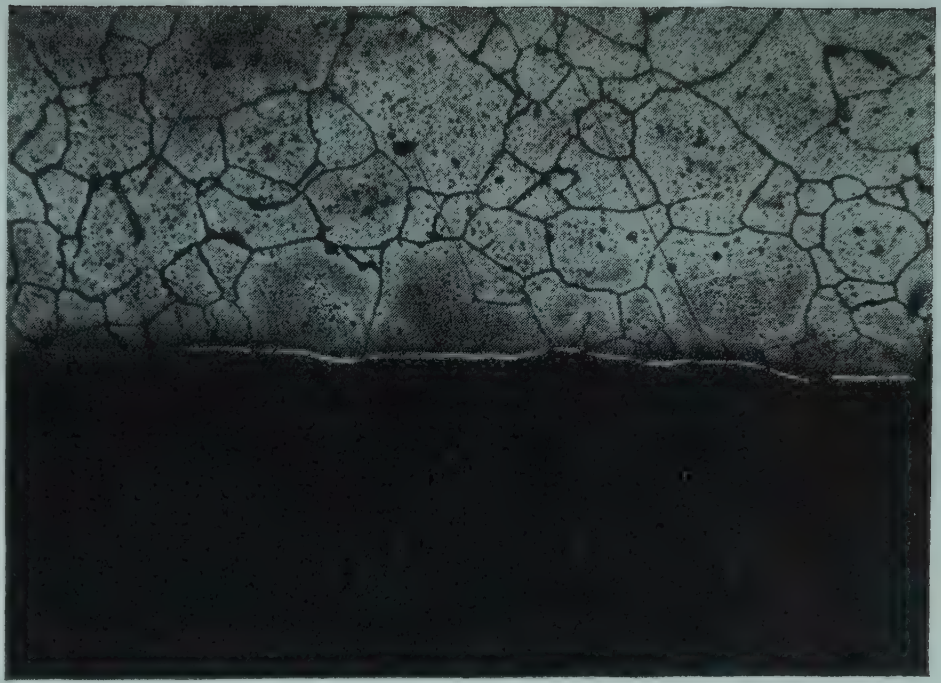

Fig. 2—Photomicrograph of the transverse section of the failed AISI 310 stainless steel tube showing the austenitic structure and the nitrided case on the inside. × 120

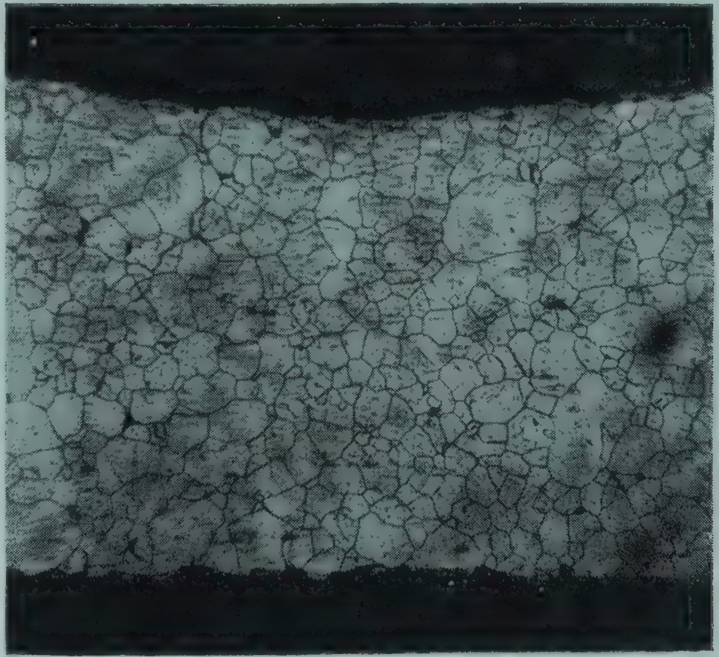

Fig. 3—Photomicrograph of the transverse section of the failed AISI 310 stainless steel tube showing the austenitic structure and the nitrided case on both the sides. × 70

the failed tube to be austenitic but extensive nitriding had occurred on the inside tube surface (Fig. 1). Thus, the metallographic structure confirmed the analytical results, hardness values and the magnetic nature of the scale. The extent of nitriding varied at different locations in the tube; at certain locations the entire thickness of the tube had undergone nitriding, while at other portions only part of the thickness had suffered nitriding. The minimum depth of nitriding was 0.8 mm. At the fractured portion, the entire thickness was observed to be nitrided. The failure was ascribed to nitriding of the stainless steel from inside because of dissociation of ammonia into atomic nitrogen and hydrogen at the steel surface, the atomic nitrogen reacting with steel to form nitride. A close study of the process conditions indicated that during service the preheater coils suffered overheating as the temperature of the preheated ammonia varied between 350° and 550°C. It thus appears that overheating has accelerated the rate of nitriding and subsequent failure.

It was recommended that AISI 304 stainless steel is not a suitable material for such service and AISI 347 stainless steel should be used.

Failure of Cracking Tubes

The cracking tubes were in operation intermittently for about 2300 hours when leakages were observed. On opening the unit, 12 out of 16 tubes were found leaking. Examination of the failed tubes showed that the tubes had failed due to thinning from inside and at the point of rupture considerable thinning had occurred. The inside surface of the tubes were covered with scales, the scales as well as the affected tubes being highly magnetic. The extent of thinning of the tubes was not uniform but varied at different locations in the tubes. The bottommost portion of the tube including the distributor appeared affected from both the inside and outside.

Analysis of the tube material gave the following results: chromium 24.5 per cent, nickel 19.6 per cent, molybdenum 0.20 per cent and aluminium 0.05 per cent.

The nitrogen content of the scale collected from inside was 3.8 per cent.

Metallographic examination of the failed tubes showed that the tubes had suffered nitriding. Except for the bottom most portion near the distributor, the tubes suffered nitriding only from inside (Fig. 2). The bottom most portion suffered nitriding from both the inside and outside (Fig. 3). The maximum depth of nitriding was 2 mm. The topmost portion of the tube which appeared unaffected was nitrided to the extent of 0.01 mm. only. It was thus concluded that the AISI 310 stainless steel tubes failed due to nitriding.

To prevent nitriding in such an environment, the most suitable material is Inconel 600. Another alloy, Incoloy alloy DS has been successfully used for catalytic cracking of ammonia and has been reported to stand a temperature of 900°C.

[Original mss. received on Jan. 6, 1973]

UDC 661.51: 547.652.1: 66.092.8

Two cases of failure which have occurred in naphtha steam reformation plants have been studied. In one case an incoloy 800 centrifugally cast header failed after only about 307 hours of service and in another a HK-40 alloy reformer tube assembly failed after about four years of service.

Failure in Reformation Plant: Some Case Studies

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In recent years, the reformation of naphtha with steam has become a very important route to the synthesis of ammonia. In this paper, some case histories of failures in the steam naphtha reformation plants are described.

Case 1

During the commissioning of new header assemblies in one of the steam/naphtha reformation section of a fertilizer factory, leaks were observed after about 307 hours of run; the temperature was about 600-650°C. In the particular plant there were two headers designated as eastern header and western header. Eastern header leaked outside the insulation box at a distance of about 9400 mm from the free end and the western header leaked inside the insulation box at a distance of about 8180 mm from the free end. The failure of the headers had occurred mostly near the weld of the pig tail and continued through the weld zone of the support saddle below the header. It was also observed that at the time of failure 6 rollers out of 10 in the eastern header and 3 rollers out of 10 in the western header were tightly fixed. The material of construction of the header as per suppliers' specification corresponded to DIN/I.4864, centrifugally cast material.

To investigate into the cause of the failure, the eastern and western headers were subjected to detailed study and compared with a new header.

Visual examination of the two failed headers did not show any apparent rusting of the surface or any other defect. The failed headers showed high magnetic pull whereas the new header was only feebly magnetic.

Analytical check up gave the following results (Table 1):

TABLE 1

Header Assembly	Percentage Composition				
	C	Mn	Si	Cr	Ni
Eastern header	0.29	1.24	0.83	17.1	38.8
Western header	0.30	1.62	0.85	17.6	38.4
New header	0.30	1.35	0.74	17.3	38.4

Mechanical tests gave the following results (Table 2).

TABLE 2

Property	Eastern Header	Western Header	New Header
UTS, kg./mm.^{2}	54.2	50.0	62.4
Elongation, %	4.2	5.0	13.6
Reduction in area, %	negligible	negligible	8.8
Hardness of inner surface, BHN	290	345	207
Hardness of Transverse section, BHN	234	227	200

The metallographic structure of both the eastern and western headers was identical, i.e. austenite with pools of ferrite, extensive carbide precipitation was observed in and along the grain boundaries (Figs. 1 and 2). The

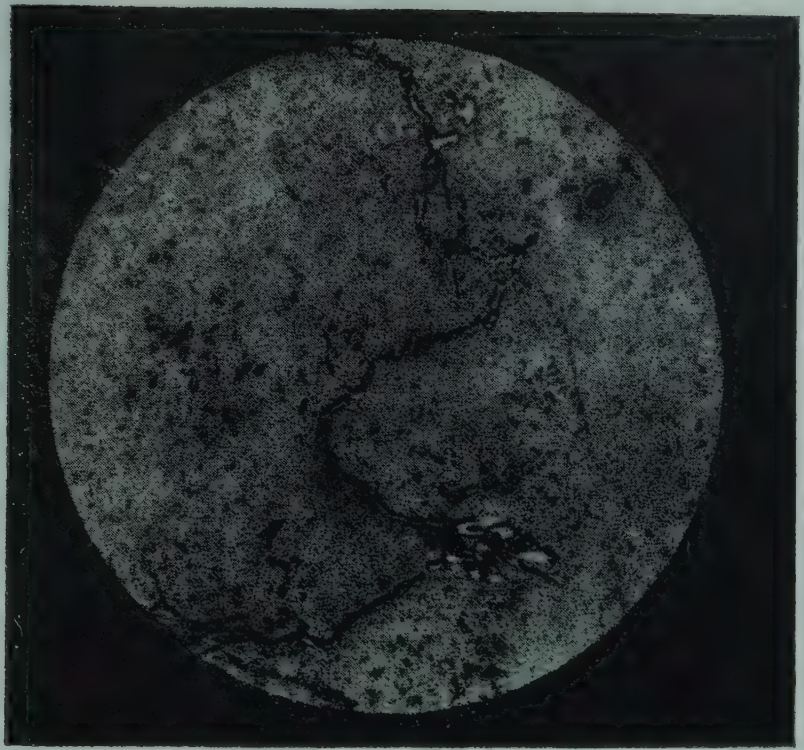

Fig. 1—Transverse section of the parent metal of Western header showing coarse austenitic structure with presence of carbide. (× 200)

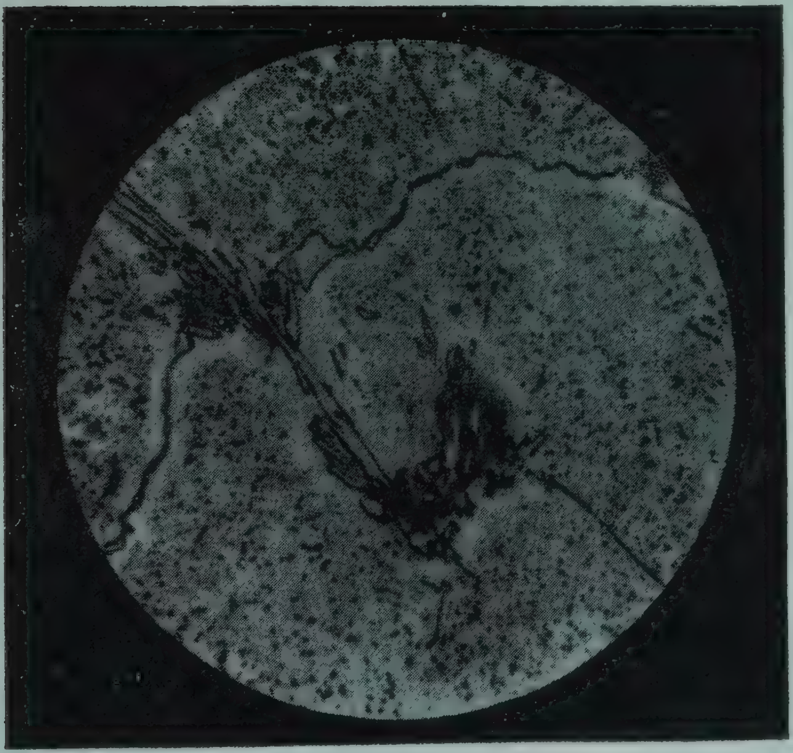

Fig. 2—Transverse section of the parent metal of Eastern header showing coarse austenitic structure with the presence of carbide. (× 270)

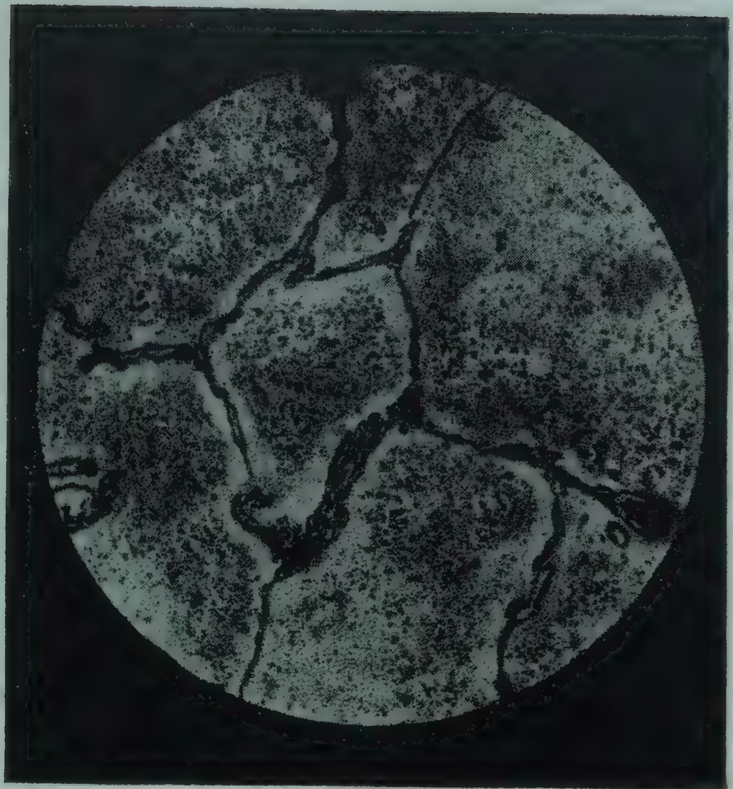

Fig. 3—Transverse section of the parent metal of New header showing its austenitic structure with the presence of carbide. (× 120)

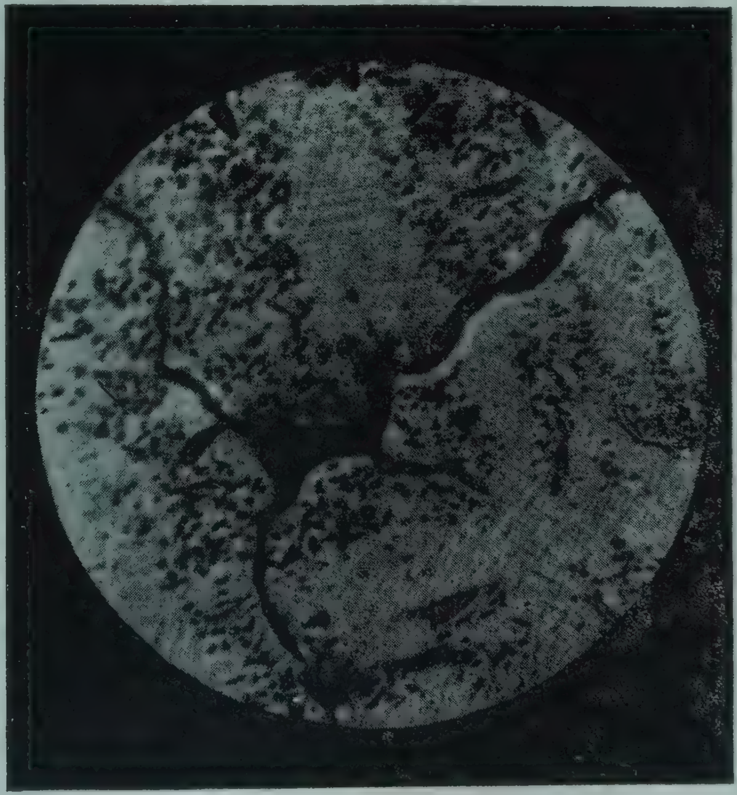

Fig. 4—Transverse section of the parent metal of cracked Western header showing austenitic structure with the presence of intergranular crack. (× 200)

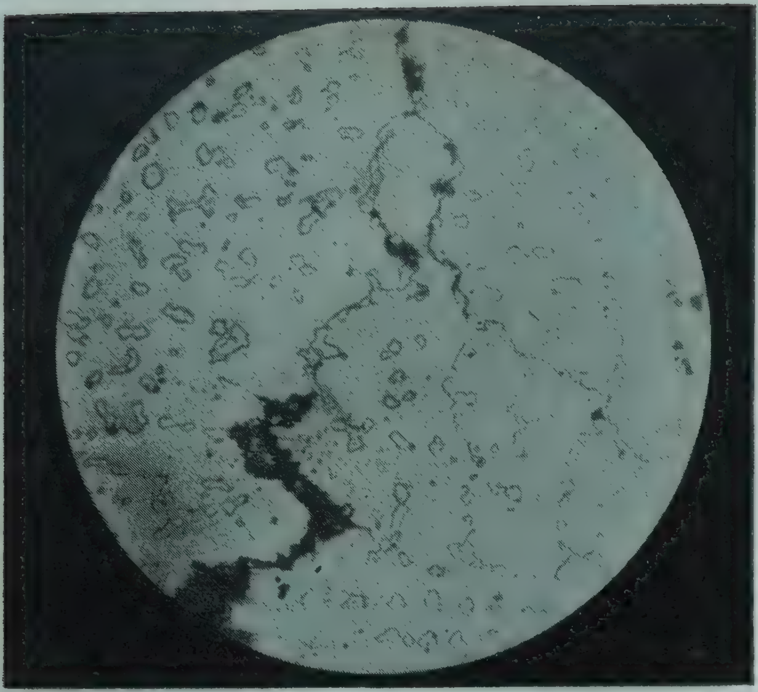

Fig. 5—Transverse section of the parent metal of the failed reformer tube showing austenitic structure with the presence of sigma phase. (× 120)

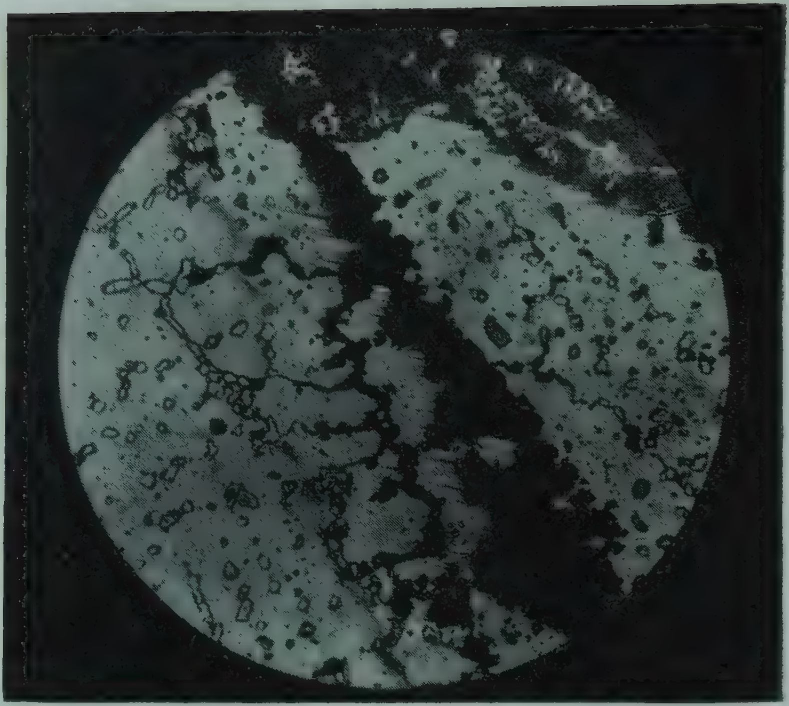

Fig. 6—Transverse section of the parent metal of the failed reformer tube showing the austenitic structure with the presence of sigma phase. There is presence of carburised layer. The pattern of crack is intergranular. (× 120)

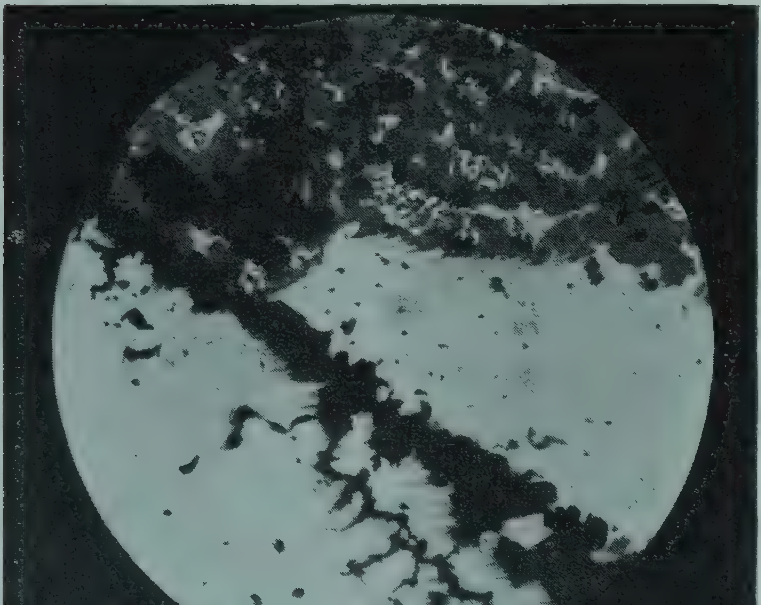

Fig. 7—Transverse surface of the parent metal of reformer tube showing carburisation in the unetched condition. (× 120)

structure of new header was austenitic with carbide precipitation (Fig. 3). The ferrite content was in the range of 19-20 per cent in the eastern header, 17-19 per cent in the western header and 2 per cent in the new header. The inner surfaces of the used headers showed a fine carburized layer. The failed portion of the used header showed fine cracks, the crack pattern being intergranular (Fig. 4).

Carburisation of the inner surface of the used headers showed that some carbon had been picked up from the gas, the chromium of the matrix reacting with the carbon to form carbide. This carbide is oxidised intergranularily more easily than the matrix as a whole. It has been reported[1] that this oxidation proceeds faster along the grain boundaries and causes microcracks.

The used headers showed high ferrite content, which indicated that in the material segregation of alloying elements had occurred. It has been reported that if an alloy contains dispersed phases which have different coefficients of thermal expansion, then on cooling, the internal stresses that are developed are relieved by generation of dislocation at the interface between the dispersed phases and the matrix. The generated dislocations would affect the creep behaviour of the material on subsequent heating.

In the present case the presence of ferrite and carbide would have caused some microcracks which could have further developed because the heating rate of the headers had been very high, viz. 360°C per hour as against the standard practice of about 50°C per hour. Moreover the number of shut-downs and start-ups had been unusually high. These factors combined together could have led to premature failure of the headers.

Moreover, while cast 18/37 alloys were commonly used in earlier reformer plants, the modern trend has been to use wrought incoloy 800 or equivalent. Its higher ductility provides greater safety against fracture.

As a preventive measure the following recommendations were made: (1) The material for such service should be Incoloy 800 or equivalent. (2) Shut-downs should be minimized. (3) The rate of heating and cooling should be about 50°C per hour.

Case 2

In another plant a reformer assembly failed after about four years of operation. The material of construction of the reformer assembly was centrifugally cast HK-40 alloy (Nominal composition C.—0.35-0.45%, Mn—2.0% max., Si—1-2%, Cr—24-28%, Ni—18-22%). Naphtha along with steam at a pressure of 12 kg./cm.^{2} and temperature 840°C flowed through the reformer assembly.

Visual examination of the assembly showed deformation and bulging. Maximum bulging was observed in the lower portions of the reformer tubes. The entire surface was covered with blackish deposit.

The metallographic structure of the reformer tube near the failed end was austenitic with coarse precipitation of carbide and sigma phase throughout the matrix (Fig. 5). Numerous cracks were observed near the failed surface and the nature of crack was intergranular (Fig. 6). Heavy carburisation of inner and outer surface was observed (Fig. 7).

The metallographic structure of the weld joining the pig tail to reducer was dendritic, with the presence of carbide precipitation and sigma phase. In this case also the inside as well outside surface appeared to be carburised. But the extent of carburisation was more in the weld zone than in the parent metal. The structure of the other weld between the reformer tube and the reducer was similar to the one described above.

The above observations indicate that the material of the reformer tube assembly had suffered carburisation on the inner as well as the outer surfaces. This results from the pick up of carbon from the gas which reacts with chromium to form chromium carbide. As explained earlier this carbide is oxidised intergranularily more easily than the matrix as a whole and may subsequently cause microcracks. Metallographic examination has confirmed the presence of sigma phase. Sigma phase develops brittle properties at ambient temperatures. During the start-ups and shut-downs it may also lead to the formation of microcracks. The microcracks once formed develop over a period of time. Thus the failure could be ascribed to carburisation and sigma phase formation. Deposition of black carbon particles on the outer surface indicated that high local heating had occurred. This overheating had actually caused deformation and bulging of the reformer tubes.

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[Original mss. received on Jan 6, 1973]

UDC 620.193: 669.141-24

Two cases of stress-corrosion failure of mild steel in fertilizer plants are described. In both the cases, the failure was ascribed to the nitrate salt dust. Remedial measures have been recommended.

Stress-Corrosion Failure of Mild Steel: Two Case Studies

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Many of the alloy systems used in production equipment in chemical plants are susceptible to stress-corrosion cracking and innumerable cases of such failures have been reported from fertilizer and other industries. In this paper, two cases of stress-corrosion failure of mild steel, which have occurred due to contamination of nitrate salt dust, have been described.

Case 1

Recently, failure of a mild steel pipe carrying liquid ammonia has been observed. A pipeline of 90 mm. O.D × 5 mm. wall thickness is provided for the transfer of liquid ammonia from ammonia storage to the nitrolimestone plant. The maximum working pressure in the pipeline is 14 kg/cm^2, which is fully lagged with slag wool. Ammonia leakage was detected at two points on this line. On opening the insulations, pipe portions having cracks were observed.

Visual examination of the failed pipe portions showed cracks on the outer surfaces. In one case, the visible crack appeared to have penetrated about half the thickness, while in the other it had penetrated the entire thickness.

Metallographic examination revealed the structure to be of a low carbon mild steel having a ferrite-pearlite structure. An examination of the cracked sample showed intercrystalline cracking pattern (Fig. 1), typical of stress corrosion failure of mild steel. A search for the orientation of the crack revealed that cracking had initiated from the outside surface. The failure was attributed to stress-corrosion failure caused by conjoint action of residual stress and nitrate salt dust from the nitrolimestone plant; the nitrate dust would have settled at portions where the insulation had cracked or gone off and with moisture would seep inside and form high local concentration of nitrate ion.

The remedial measure suggested was to cover the exposed portion of the pipeline with impervious coating to eliminate contact with outside environment.

Case 2

A 4″ diam. steam header failed in an ammonium nitrate plant after a short period of service. The service conditions were: Fluid—Steam; temperature—165°C.; and pressure—6 kg/cm^2. The header was insulated with glass wool and lagged with aluminium sheets. The plant was under trial run; so it was operated only intermittently.

Visual examination of the failed samples showed cracks on the outside surface. Some of the visible cracks appeared to have penetrated to about half the thickness. Metallographic examination of the failed portions' showed the structure to be ferrite-pearlite with numerous cracks, the pattern of cracking being intercrystalline (Figs. 2 & 3). A search for the orientation of the cracks revealed that in all cases the cracks had initiated from the outside surface, some of which had penetrated through the entire thickness while others had penetrated only to a certain distance. Chemical analysis of the used mineral wool showed contamination with high contents of nitrate and ammoniacal nitrogen; the contents of nitrate and ammoniacal nitrogen being much less in the unused mineral wool.

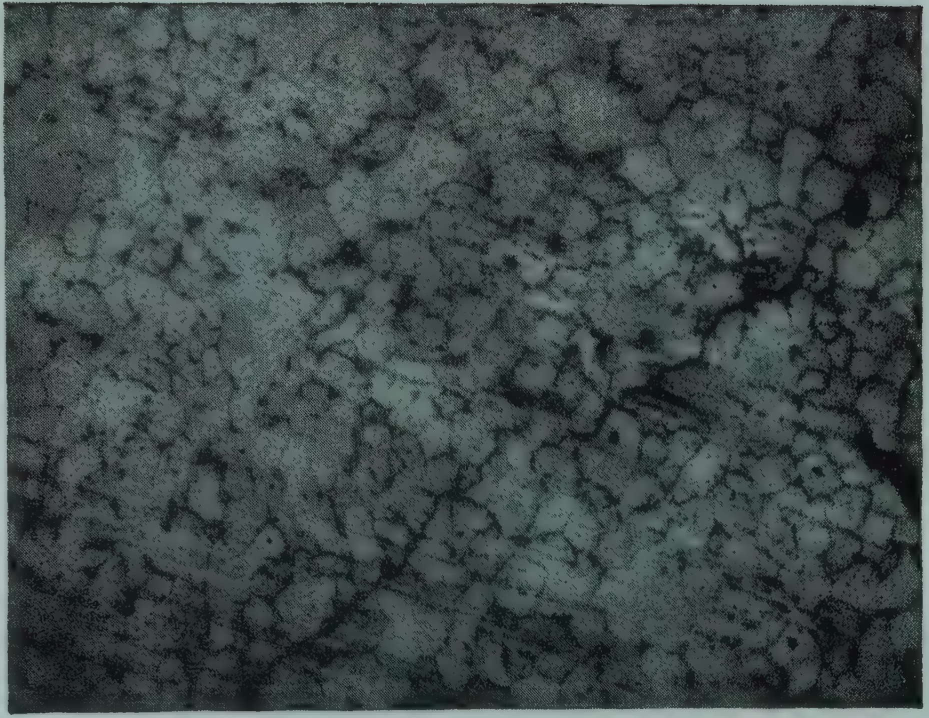

Fig. 1—Photomicrograph of the cracked mild steel liquid ammonia line showing inter crystalline cracking pattern. (× 340)

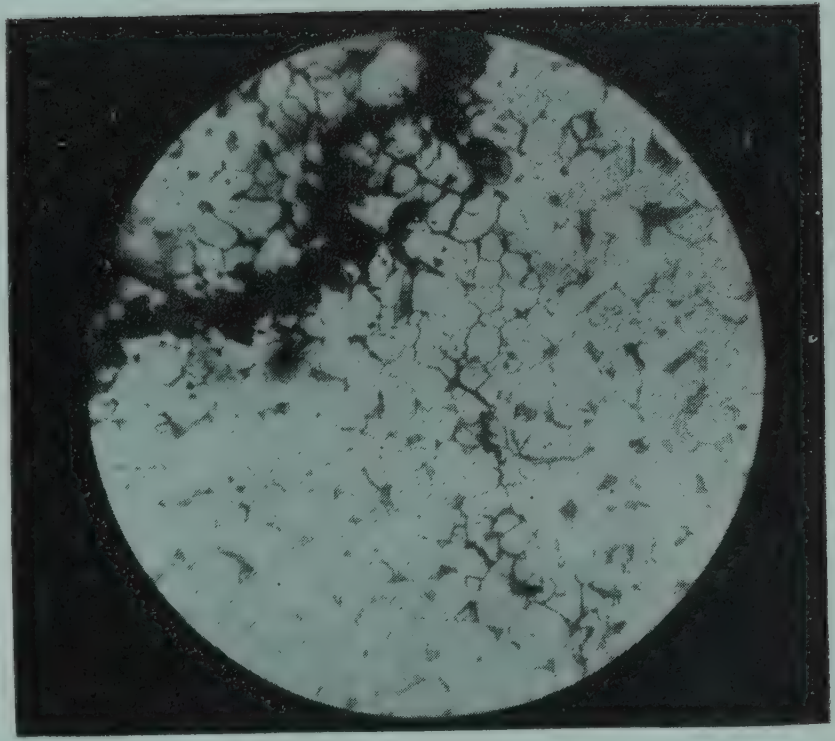

Fig. 2—Photomicrograph of the failed mild steel steam header showing intercrystalline cracking pattern. (× 200)

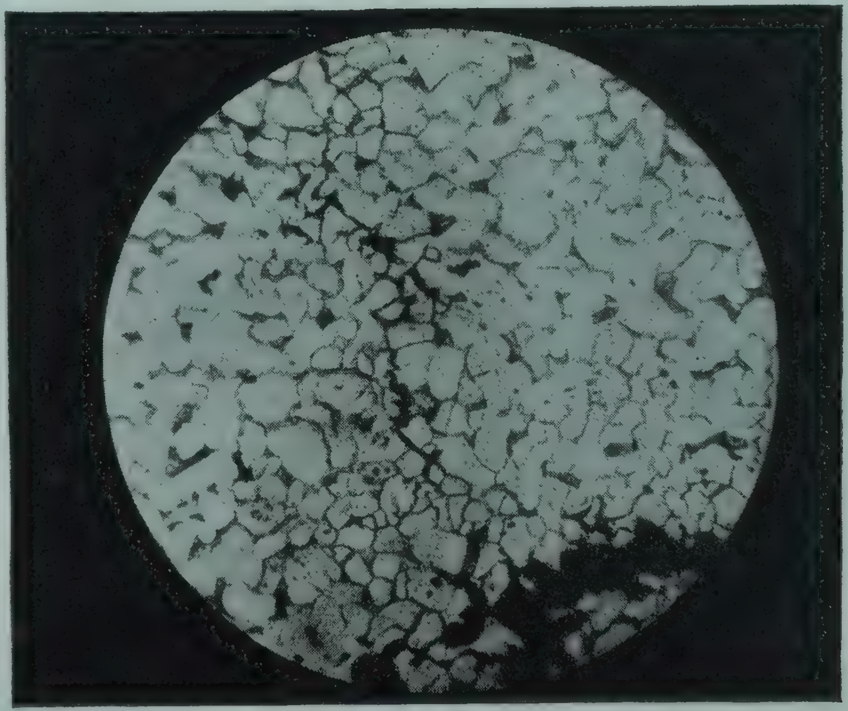

Fig. 3—Photomicrograph of the failed mild steel steam header showing intercrystalline cracking pattern. (× 200)

Mild steels have been reported to suffer intercrystalline attack in nitrate media. Thus, it was concluded that during service, dust containing ammonium nitrate along with water had seeped to the mild steel surface, resulting in high local concentrations and causing stress-corrosion failure of the mild steel header.

As a remedial measure, it was recommended that special efforts should be made to keep the outside of the steam header free from deposits of ammonium nitrate and other salts.

[Original mss. received on March 25, 1973]

UDC 546.74: 541.67: 541.128

Thermomagnetic studies on three samples—nickel hydroxide, nickel carbonate monohydrate and nickel oxalate dihydrate—have been presented. The observed magnetic moments at 25°C for nickel ions in these compounds lie within 3.1±0.1 B.M. and confirm the molecular formulae of the precipitates.

Magnetic Properties of Some Nickel Compounds of Catalytic Importance

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Introduction

The role of nickel as a catalytic element is well-known[1] and the use of different magnetic techniques[2] to evaluate the electronic properties of the metal in the catalysts are also recognized. In this report, the authors have attempted to focus on the inherent magnetic dilutions or dispersions, which a number of catalytically important nickel compounds possess after precipitation from nickel nitrate solutions. In the evaluation of the supported catalyst by magnetic techniques, sometimes the reference data on the unsupported catalytic component become helpful and in this respect lies the usefulness of the present study.

Experimental

Preparation of the Samples: A detailed procedure on the preparation of samples and the DTA and TGA studies has been communicated earlier[3]. On the basis of the thermogravimetric analyses, the precipitates can be classified as follows;

(a) **Nickel hydroxide**—Two samples were prepared by reacting with ammonia and sodium hydroxide. The sample precipitated with sodium hydroxide contains 0.55 per cent sodium which was estimated by the flame photometric method.

(b) **Nickel carbonate monohydrate**—Two samples were prepared by the action of ammonium bicarbonate and ammonium carbonate at 60°C with nickel nitrate solutions.

(c) **Nickel oxalate dihydrate**—This was precipitated with ammonium oxalate and washed thoroughly to make it oxalate-free.

Magnetic Measurements: The magnetic susceptibility values of these samples were measured by a precision two-section helical quartz spring Faraday-type magnetic balance.[4] A weighed amount of the sample (approx. 20 mg) was heated in the magnetic balance at 120°C for $\frac{1}{2}$ hr. to drive out the moisture and then magnetic measurements were taken.

Results and Discussion

The temperature dependence of a paramagnetic material is best represented by the Curie's Law,

$$X_M = \frac{C}{T} \qquad \dots \quad (1)$$

where X_M = Molar susceptibility of the magnetic material,
and C = Curie constant, which is related to the oxidation state of the magnetic ion.

A plot of temperature versus reciprocal specific magnetic susceptibility gives a straight line, which passes through the origin for a purely paramagnetic specimen and makes a positive or a negative intercept on the temperature axis according to the ferromagnetic or antiferromagnetic nature of the sample. In Fig. 1, the obedience of the Curie's law by the nickel compounds under study is shown. Thermomagnetic studies in the range 25 to 130°C have been made to avoid the loss of water of crystallization and decomposition of the compounds. The complete magnetic data and the biography of the precipitates are given in Table 1. The effective magnetic moments were calculated using the formula

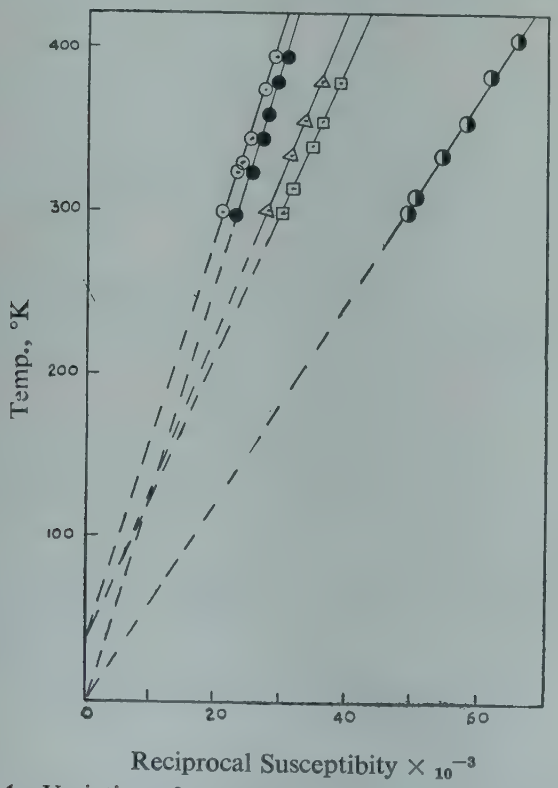

Fig. 1—Variation of magnetic susceptibility with temperature,
Nickel hydroxide:
⊙ —Precipitant Ammonia.
● —Precipitant Sodium hydroxide.
Nickel carbonate monohydrate:
△ —Precipitant Ammonium carbonate.
⊡ —Precipitant Ammonium bicarbonate.
Nickel oxalate dihydrate:
◐ —Precipitant Ammonium oxalate.

$$\mu_{eff} = 2.84 \sqrt{X_M (T - \triangle)} \qquad \dots \quad (2)$$

where $\triangle$ = observed Weiss constant.

The observed magnetic moments at 25°C correspond to two unpaired d-electrons present in a nickel atom and suggest a divalent electronic state of nickel in these compounds.

The magnetic parameters (Table 1) suggest that all the five precipitants are equally good for catalyst preparation.

TABLE 1—MAGNETIC PROPERTIES OF THE NICKEL COMPOUNDS

Material	Precipitant	Specific Susceptibility at 25°C × 10⁶ e.m.u.	Magnetic Moment at 25°C B.M.	Weiss Constant, °K
$Ni(OH)_2$	Ammonia	48.86	3.1	40
$Ni(OH)_2$	Caustic Soda	45.12	3.2	Zero
$NiCO_3 . H_2O$	Ammonium Carbonate	36.70	3.2	40
$NiCO_3 . H_2O$	Ammonium Bicarbonate	34.24	3.1	40
$NiC_2O_4 . 2H_2O$	Ammonium Oxalate	20.51	3.0	Zero

By the action of ammonium carbonate or ammonium bicarbonate with nickel nitrate solution, nickel carbonate monohydrate is precipitated at 60°C instead of the nickel basic carbonate. This was first established by TGA studies[3] from this laboratory and now confirmed by magnetic data.

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[Original mss. received on May 28, 1973]

UDC 631.8: 546-171-1.002.2

Influence of the additives of nitrogenous, phosphatic and potassic components on the ammonia losses of DAP at 80°C has been studied. The extent of ammonia loss showed marked variation depending on the nature of the additives.

Extent of Ammonia Loss during Processing of DAP-based N-P or N-P-K Formulations

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Ammonium phosphate has become very popular in recent years and its production is rapidly increasing. A combination of DAP (diammonium phosphate) with other fertilizers is a natural route to formulating high analysis N-P and NPK grades with 50-60 per cent total plant food content. A knowledge of the thermal stability of these high analysis fertilizers is, therefore, essential. Guerrant and Brown[1] studied the thermal decomposition of high analysis fertilizers based on ammonium phosphates and showed that significant nitrogen losses could occur during drying and storage from grades formulated with DAP and urea. Moreover, the production of granular fertilizer of NPK, like DAP+Urea needs thorough drying, which is comparatively difficult than that of DAP (18-46-0) as DAP with a moisture content of 1.5 per cent stores well in bulk and in bags without any conditioner. But when ammonium nitrate or urea is present along with DAP, the fertilizer has to be dried to a lower moisture content to keep it free flowing during its storage and transport. Drying to the lower moisture content necessitates a higher retention time in the drier, in which rigorous control of the temperature of the drying flue gas is exercised to avoid nutrient loss.

Besides this, the compatibility relationships between most of the commonly used fertilizer materials with DAP need to be probed. Tests made by Beeson[2] showed that addition of limestone to DAP results in high ammonia losses even at 30°C. MacIntire and Sanders[3] found negligible ammonia loss from 4 to 1 mixtures of 100 mesh (B.S.S.) calcitic and dolomitic limestones with nitrophoska that contained about 60 per cent DAP and 40 per cent ammonium nitrate. This was found true both for mixtures containing 6 per cent moisture and completely air-dried products. Thompson *et al*[4] have shown that addition of various supplements did not cause any appreciable dissociation of ammonia from DAP. However, in their study it was not the case with DAP-AN and DAP-Urea mixture with N_2:P_2O_5 ratio between 0.75—1.0.

This investigation was undertaken to determine the losses occurring in the drying of DAP along with other nitrogenous, phosphatic and potassic ingredients normally used for making multi-nutrient fertilizers.

Experimental

DAP and all other reagents used in this experiment were of BDH (AnalaR) quality. They were dried over sulphuric acid in a desiccator and used without recrystallization.

5 g. of DAP was taken in a 10 cm. diam. glass petri dish and allowed to absorb moisture in a water desiccator. The DAP (moist) was then mixed with other reagents and transferred to a reaction vessel.

The experimental set up was the same as in the study of urea hydrolysis[5] with only the alkali-bubbler placed immediately after the reaction vessel removed. Ammonia liberated was absorbed in a known volume of sulphuric acid (dil). of known strength. The liberated ammonia was titrated with caustic soda (dil.).

Results and Discussion

The thermal decomposition of reagent grade DAP was measured at 80°C .The moisture present was 5 per cent and the time periods were 30 and 120 minutes. The results are tabulated in Tables 1 and 2.

TABLE 1

[Temp. 80°C; Time 30 min.; Moisture 5 per cent]

System	Amount	% NH_3
DAP	—	0.11
DAP+$(NH_4)_2SO_4$	$N:P_2O_5 = 1:1$	0.12
DAP+NH_4HO_3	,,	0.18
DAP+MAP	—	0.10
DAP+Urea	$N_2:P_2O_5 = 1:1$	0.11
DAP+KNO_3	,,	0.15
DAPK+KCl	$P_2O_5: K_2O = 1:1$	0.19
DAP+NH_4NO_3+KCl	$N_2: P_2O_5: K_2O = 1:1:1$	0.30
DAP+Urea+KCl	,,	0.29

TABLE 2

[Temp. 80°C; Time 120 min.]

System	Moist., %	Amount	% NH_3
DAP	5	—	0.38
DAP	10	—	0.50
DAP+NH_4NO_3	5	$N_2: P_2O_5 = 1:1$	0.71
DAP+NH_4NO_3	10	,,	0.76
DAP+NH_4NO_3	,,	$N_2: P_2O_5 = 1:2$	0.73
DAP+$NaNO_3$	,,	$N_2: P_2O_5 = 1: 1$	0.63
DAP+KNO_3	,,	,,	0.61
DAP+Urea	,,	,,	0.64
DAP+KCl	,,	$P_2O_5: K_2O = 1:1$	0.84
DAP+NH_4NO_3+KCl	,,	$N_2: P_2O_5: K_2O =1:1:1$	1.24
DAP+Urea+KCl	,,	,,	1.24

Margineanu *et al*[6] showed that the decomposition rate of DAP was influenced directly by the partial pressure of water vapour present in the air. The energy of activation of DAP decomposition decreases in the moist air and the condensed moisture on the DAP surface gave rise to hydrolysis. In Table 2, the decomposition of DAP and DAP ammonium nitrate systems in presence of 5 and 10 per cent moisture for 120 min. are given: it shows that a little increase in the decomposition does occur with the increase of moisture.

Except in a few cases, DAP drying is not attended with an increased evolution of ammonia. The extent of decomposition is extremely small but in the presence of some salts it is comparatively high. Contrary to expectation, there was almost no evolution of ammonium chloride fumes in $(NH_4)_2HPO_4-NH_4Cl$ system. The extents of decomposition of DAP ammonium nitrate (1:1) and DAP-Urea (1:1) are only 0.18 and 0.11 per cent (same as DAP), and 0.76 and 0.64 per cent respectively. These are much smaller than those estimated by Thompson *et al*[4] and more or less conform to the stability value of 30-10-0 grade made up of DAP (15 per cent) and ammonium nitrate studied by Guerrant and Brown[1]. By decreasing the amount of ammonium nitrate, there was no appreciable change in the rate of decomposition. As against this background, the results of DAP potassium chloride mixture ($P_2O-K_2O = 1:1$) were somewhat different. Guerrant and Brown[1] showed that the thermogram of 90 per cent of reagent grade DAP with 10 per cent potassium chloride was closely parallel to the DAP curve. The solubility study of DAP-KCl-H_2O[7] indicated that DAP was salted out so much so that there would be less evolution of ammonia. In the systems of DAP-NH_4NO_3-KCl and DAP-Urea-KCl, the extent of decomposition seems to be the cumulative effects of two additives.

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[Original mss. received on April 27, 1973]

UDC 661.5: 547.652.002-2

Due to the nonavailability of the right type of coal and the aging of the coke ovens the quality and quantity of coke oven gas make was low and the production of synthesis gas from the Gas Reforming Plant of the Sindri Fertilizer Factory came down to a very low level. During 1970-71, the situation came to such a pass that it was difficult to maintain even the lowest rate of production in the plant. Under such circumstances, a scheme was worked out to boost up production by injecting naphtha along with hydrocarbon fraction. Therefore, an experiment on injecting naphtha into the feed gas of the existing cracking furnace was undertaken. The results were reassuring and fruitful.

This article, after outlining the hazards associated with naphtha injection, describes the progress of the experiment through all its five different stages, giving the problems encountered and their solutions. This scheme gave a production boost of about 40 t.p.d. ammonia and significant improvement in the plant operating conditions. A brief description of the existing hydrocarbon cracking unit of the plant and a block diagram for the process flow scheme in the Gas Reforming Plant of the fertilizer factory are also given.

Naphtha Injection Boosts Ammonia Production

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Fertilizer Corporation of India Ltd., Sindri, Bihar

The Gas Reforming Plant of FCI Ltd. Sindri Unit was designed to produce synthesis gas equivalent to 189 tonnes/day of ammonia by processing 11200 Nm^3/h of coke oven gas, produced from the coke oven plant using high volatile weakly caking Raniganj coal and utilizing the stamping process developed by M/s Carl Still of West Germany. However, during the early period of operation, the stamping process failed and consequently, the ovens had to be operated in the conventional method of top charging and utilizing mostly good quality metallurgical coal. The coke oven gas was partly utilized for underfiring due to short supply of lean gas. Subsequently, two more lean gas producers were added and the coke oven batteries started getting fired only by lean gas. Thus, the entire coke oven gas was released for ammonia production, and its availability was assessed to be 8000 – 9000 Nm^3/h, which could produce synthesis gas equivalent to 150 – 160 tonnes/day of ammonia.

In 1965, a scheme for a naphtha reformation plant was submitted to supplement the gas shortage, and considering the possibility of further deterioration in the performance of coke ovens, the capacity of the plant was recommended as reformed gas equivalent to 60 tonnes per day ammonia. The naphtha reformation unit was installed and commissioned in 1969 and simultaneously, the water scrubber packings were changed to higher size and one MEA scrubber was installed.

Even after the implementation of the supplementary gasification scheme outlined above, the plant was unable to operate at its design capacity. In 1970, an investigation was conducted to detect the lacunae which revealed that wide variation in the quality as well as quantity of coke oven gas was mainly responsible for limiting the production rate. This variation upsets the cold boxes completely and consequently the whole system gets unbalanced. Some efforts were made to minimize the fluctuations in the quality and quantity of coke oven gas, which yielded hardly any improvement. Subsequently, the coal supply position deteriorated further and cracks were detected in a number of ovens.

All these factors led to the production of all-time low quality and quantity of coke oven gas. At that time, about 5000 Nm^3/h of gas was available for processing in the Gas Reforming Plant. This had aggravated the situation to such an extent that it was difficult to maintain even the lowest rate of production in the plant. The available gas quantity was inadequate to run two fractionation units, and without running them the available gas from the naphtha reformer could not be utilized. Under such circumstances, a serious thought was given to find out ways to stabilize and to boost up the production in the Gas Reforming Plant.

A scheme was, therefore, submitted to the Sindri Unit Management for carrying out an experiment of injecting naphtha into the hydrocarbons feed to the cracking furnaces, so that the unutilized capacity of the cracking furnaces as well as the surplus oxygen from the oxygen plant could be fully utilized. Only naphtha was considered for injection because the existing facilities for its handling and purification could enable the authors to get results within a very short time.

With the approval of the scheme by the Sindri Unit Management, the experiment was undertaken on top priority. Naphtha injection was started at a very low rate using sweet naphtha from the existing steam-naphtha reformation plant and subsequently the rate was increased to 1400 kg/hr. using raw naphtha. This resulted in an additional ammonia production over 40 to 45 tonnes/day. Apart from the production boost, the injection stabilized the operating condition of the plant. A brief description of the existing hydrocarbon cracking unit, the details of the experiment conducted and the results achieved are described below.

Existing Cracking Unit

The cryogenic separation of coke oven gas is carried out in the gas fractionation Boxes and the resulting hydrocarbon fraction is cracked in catalytic autothermal cracking furnaces at low pressure in presence of oxygen and steam (Fig. 1).

The unit consists of two parallel streams capable of being run independently. The feed gas is divided into two portions, one for each of the streams. It is preheated by the hot cracked gas in the feed preheaters, steam is added to it and finally the hydrocarbon: steam mixture joins oxygen stream in the mixers below each furnace. The oxygen coming from the air fractionation unit is supplied to the mixers after boosting its pressure with blowers. The ratios hydrocarbons/oxygen and hydrocarbon/steam are adjusted to maintain the catalyst bed temperatures and get the necessary percentages of methane and carbon dioxide in the outlet gas.

The cracked gas at the furnace exit is at 750 – 800°C and its heat is recovered successively in steam superheater, boiler, feed preheater and the economizer. The gas exit economizer is at about 85 – 90°C. The gas is sent to the gas holder after being cooled to 35 – 40°C in a direct cooler.

Automatic safety devices are provided to trip the unit and to safeguard it in any emergency. The safety system, incorporating magnetic valve (SV_1), magnetic vent valve (SV_2) and the steam flushing, is shown in Fig. 2. If any dangerous situation develops, the magnetic valve SV_1 closes to cut off the oxygen to the oven

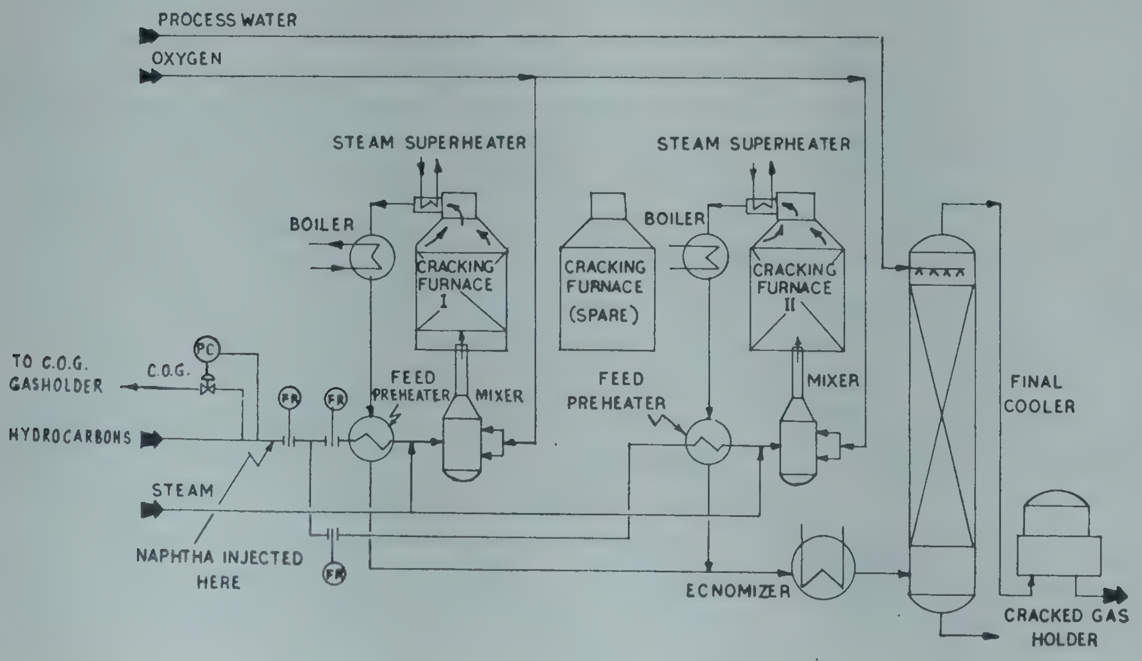

Fig. 1—Flow Scheme of the Hydrocarbon Cracking Unit

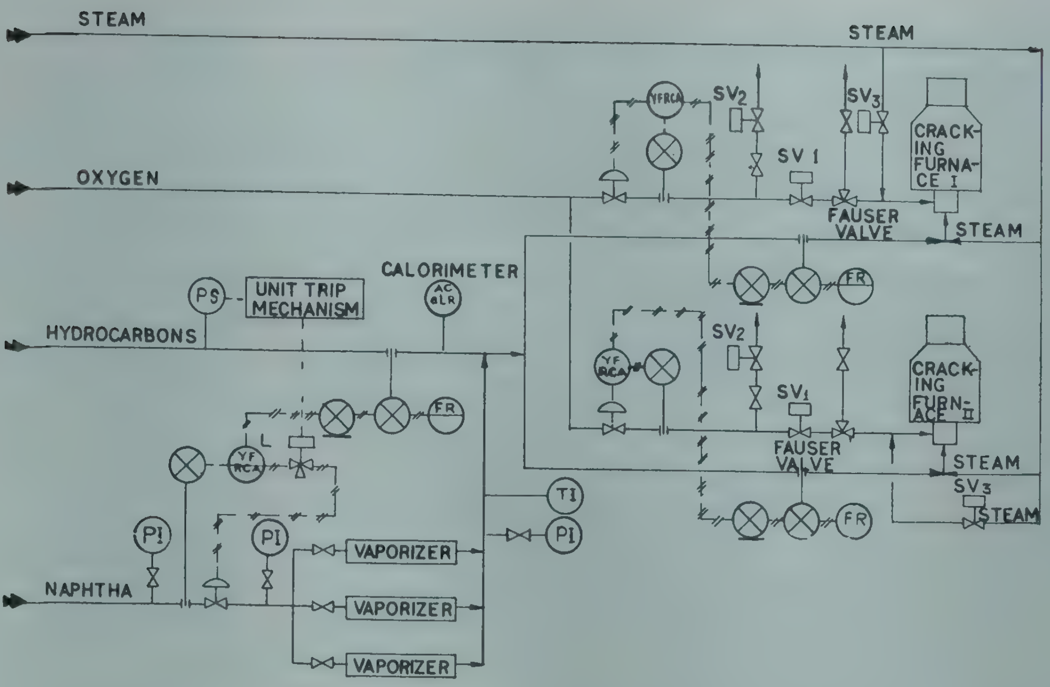
STEAM
STEAM
SV2
SV3
CRACKING FURNACE I
SV 1
OXYGEN
FAUSER VALVE
STEAM
CALORIMETER
PS
UNIT TRIP MECHANISM
HYDROCARBONS
FR
SV2
SV1
CRACKING FURNACE II
FAUSER VALVE
STEAM
SV3
STEAM
TI
PI
PI
PI
FR
FR
VAPORIZER
VAPORIZER
VAPORIZER
NAPHTHA

Fig. 2—Instrumentation Scheme for Cracking Section with Naphtha Injection

and the steam flushing valve SV$_3$ opens to flush oxygen line with steam (Fig. 2). Thus, the whole safety system acts to prevent the backfire.

The hydrocarbon cracking furnace is of unconventional design (Fig. 3). The hydrocarbon: steam: oxygen mixture introduced at the bottom gets distributed through two layers of mullite balls arranged in front of a refractory cone. The catalyst with varying nickel content is packed as shown in the sketch, it was originally supplied by M/s. Haldor Topsoe and subsequently replaced by the FCI catalyst. The bottommost catalyst layer containing 2.5 per cent nickel catalyst is hydrogenation zone. This is followed by a 5 per cent nickel catalyst layer which constitutes the partial oxidation zone. The 10 per cent nickel catalyst packed in the topmost layer acts as the reforming catalyst. The hydrogenation, cracking and reformation reactions take place in succession as the reaction mixture rises from bottom to the top of the catalyst bed. The cracked gas coming out at the top enters the steam superheater and gets cooled through the process steps described earlier.

Experimental

The possible adverse consequences of naphtha injection were kept in mind while undertaking the experiment. The presence of naphtha in the feed to the cracking furnace could lead to the following hazardous conditions: (i) The mullite balls are nothing but hot ceramic bodies. There was fear of carbon deposition on their surface soon after naphtha comes into contact with them which would have blocked the whole gas passage; (ii) if naphtha is injected in conjunction with a low hydrocarbon flow rate, there is always danger of a backfire due to the low feed gas velocity in the inlet pipe; (iii) naphtha being a concentrated fuel, the specific oxygen to feed gas ratio has to be kept higher. The existing oxygen ratio control system operates on the

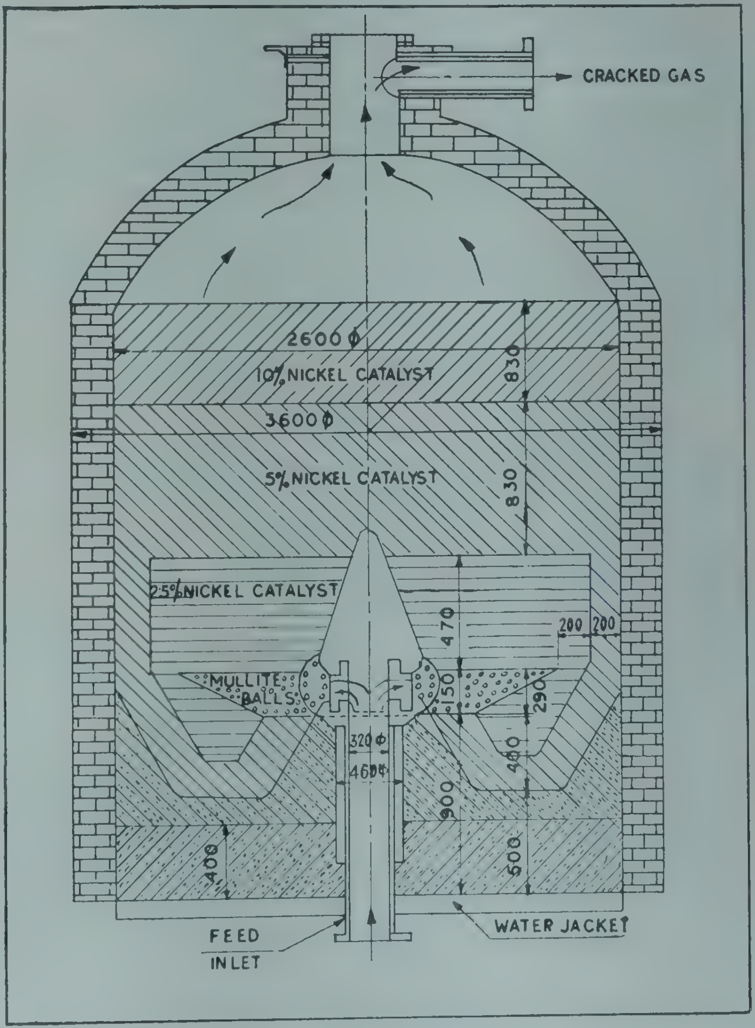
CRACKED GAS
2600 ϕ
10% NICKEL CATALYST
830
3600 ϕ
5% NICKEL CATALYST
830
2.5% NICKEL CATALYST
470
200
200
MULLITE BALLS
150
290
320 ϕ
460 ϕ
900
460
400
500
FEED INLET
WATER JACKET

Fig. 3—Hydrocarbon Cracking Furnace of the Gas Reformation Plant, FCI Ltd., Sindri Unit

basis of volumetric flow which is very small for naphtha as compared with the total flow of hydrocarbons. In case of sudden stoppage of naphtha, the oxygen-to-hydrocarbon ratio will be very high and there are chances of an explosion or this may result in fusion of the catalyst due to the resultant high temperatures; (iv) in case of a sudden stoppage of hydrocarbons flow, oxygen will be cut off immediately. Then, naphtha alone may continue for sometime through the catalyst bed. This may cause coke formation and the complete blockage of catalyst; and (v) the injection of raw naphtha was also unavoidable since the surplus capacity of sweet naphtha from the existing hydrofining section was very small. There were apprehensions that the sulphur in raw naphtha might poison the catalysts in cracking furnaces, and shift reactors. This could also have adverse effect on the performance of Urea Plant due to high sulphur in CO_2 gas.

Being fully aware of these dangers, it was decided to conduct the experiment in a phased manner (Fig. 4) and with great caution. The operating conditions during each phase are given datewise in Table 1. To start with, sweet naphtha from the sweet naphtha pump suction at about 12 kg/cm²g pressure and about 70°C was injected into the hydrocarbon line feeding cracking furnace I through a flow control valve. This first phase of the experiment injecting liquid naphtha upto 75 kg/hr. resulted in satisfactory process conditions but it was observed that the higher fractions of naphtha remain unvaporized and have to be drained away. To avoid this difficulty, the injection of naphtha in the vaporized form was considered. To achieve this end, an exchanger from the scrap yard was picked up to be used as a naphtha vaporizer. The second phase of the experiment consisted of injecting sweet naphtha through this vaporizer upto the maximum rate of 300 kg/hr. A careful watch was maintained over catalyst bed temperatures, pressure drop and exit gas analysis as injection rates were successively increased.

No condensation of naphtha was noticed from any of the drains but, the injection rate could not be stepped up further because that would have created limitation for the full capacity operation of naphtha reformer. So, further increase in the naphtha injection rate was considered with the use of raw naphtha only.

Before trying the injection of raw naphtha, the vaporizer in use was replaced by another from scrap yard since the latter could stand slightly higher steam pressure. The third phase of the experiment consisted of injection of raw naphtha vapour at about 150°C to an extent of 250 kg/hr. in the COMMON HYDROCARBON HEADER. Raw naphtha injection at this low rate was continued for observing the pressure drop across the catalyst bed, soot formation, if any, possible naphtha slippage and percentages of carbon dioxide and methane in the outlet gas. The observation showed practically no difficulty.

The vaporizers picked up from the scrap yard could not afford naphtha injection rates higher than 300 kg/hr. Therefore, a new vertical vaporizer was designed by the authors in order to try the higher injection rates. This

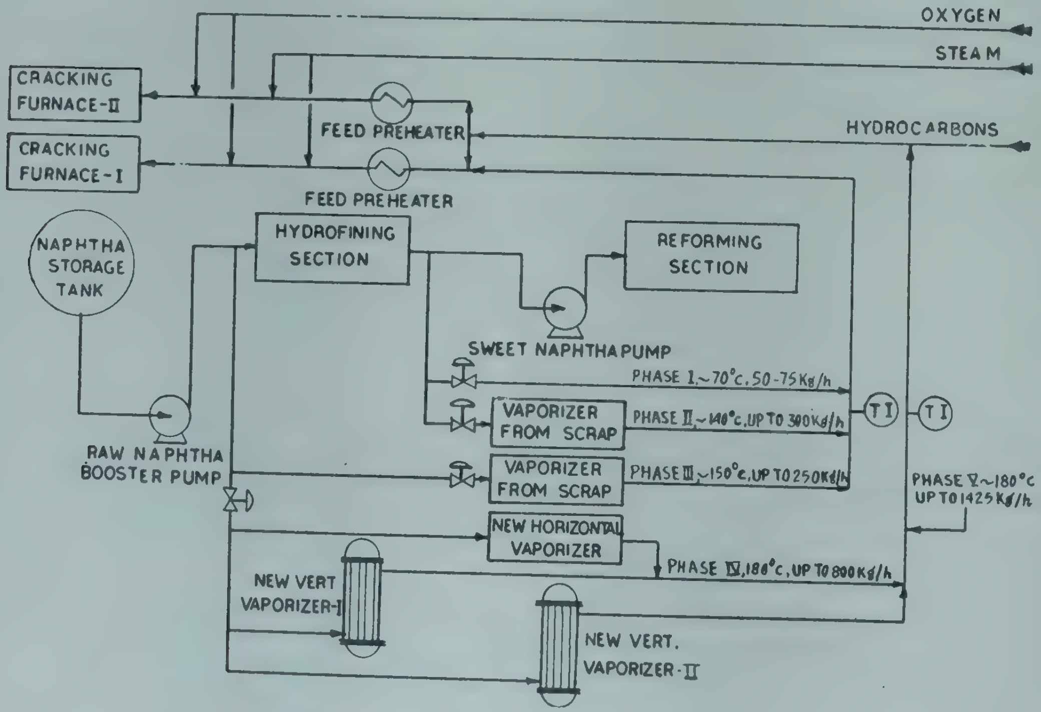
OXYGEN
STEAM
CRACKING FURNACE-II
CRACKING FURNACE-I
FEED PREHEATER
HYDROCARBONS
FEED PREHEATER
NAPHTHA STORAGE TANK
HYDROFINING SECTION
REFORMING SECTION
SWEET NAPHTHA PUMP
PHASE I~70°c. 50-75Kg/h
VAPORIZER FROM SCRAP
PHASE II~140°c, UP TO 300Kg/h
T I
T I
RAW NAPHTHA BOOSTER PUMP
VAPORIZER FROM SCRAP
PHASE III~150°c, UP TO 250Kg/h
PHASE V~180°c UP TO 1425Kg/h
NEW HORIZONTAL VAPORIZER
PHASE IV, 180°c, UP TO 800Kg/h
NEW VERT VAPORIZER-I
NEW VERT. VAPORIZER-II

Fig. 4—Different Phases of Naphtha Injection Experiment

TABLE 1—REPRESENTATIVE PLANT OPERATING CONDITIONS WITH NAPHTHA INJECTION

Phase of the Expt.	Date	C.V. of Hydrocarbon Feed	Flow Rate of Hydrocarbons	Naphtha		Oxygen Flow Rate	Steam Flow Rate	Cracked Gas Make	Max. Bed Temp		Cat. Bed. △p		Cracked Gas Analysis, % By Vol.					No. of Units Running	Remarks
				Injection Rate	State				Unit I	Unit II	Unit I	Unit II	H_2	CO	CO_2	CH_4	N_2		
		Kcal/NM³	NM³/hr.	kg/hr		NM³/HR	kg/hr	NM³/hr	°C	°C	MM.HG	MM.HG							
I	23.6.71	7025	1825	50	Sweet Liquid	630	616	7833	930	895	20	25	57.2	22.2	8.6	4.6	7.4	I+II	Naphtha Injection started on 23.6.71 at 11.15 A.M. to Cracking Unit I @ 50.5 KG/HR
	24.6.71	7200	1570	75	,,	697	652	8417	940	920	22	35	57.6	24.6	7.6	2.8	7.4	I+II	
II	29.6.71	5375	2200	100	Sweet Vapour	1077	839	5021	910	—	50	—	63.2	24.4	8.6	1.2	2.6	I	Vaporizer from Scrap yard taken in line on 29.6.71 at 9.00 A.M.
	30.6.61	5275	2465	150	,,	1135	852	5762	N.A.	—	48	—	58.4	27.0	7.4	1.8	5.4	I	
	3.7.71	5737	2305	200	,,	1050	842	4776	950	—	40	—	57.4	27.2	8.0	3.0	4.4	I	
	6.7.71	7987	2640	300	,,	1240	969	6536	930	—	45	—	58.6	26.4	7.6	3.0	4.4	I	
III	11.7.71	7475	1670	250	Raw Vapour	832	756	7568	890	930	20	43	57.2	25.6	8.2	3.0	5.2	I+II	Injection of Raw Naphtha resorted at 11.15P. M. on 10.7.71, increased to 200 Kg./Hr. By 3.00 A.M. on 11.7.71 and to 250 Kg/Hr. by 10.00 A.M. of 11.7.71
	13.7.71	7837	1975	200	,,	987	752	5687	850	—	40	—	58.4	25.2	8.0	3.0	5.4	I	
	14.7.71	6600	1990	150	,,	870	750	3572	910	—	38	—	54.0	25.6	8.0	3.4	9.0	I	
IV	15.7.71	6500	3650	400	,,	1755	1515	9430	900	915	35	38	57.2	27.0	6.8	2.8	6.2	I+II	
	16.7.71	6637	3615	500	,,	1752	1719	9591	900	900	29	27	57.0	27.2	7.6	2.0	6.2	I+II	
	24.7.71	6050	3673	600	,,	1753	1476	10242	915	910	32	28	58.8	26.6	7.0	2.2	5.4	I+II	
	25.7.71	6300	3650	700	,,	1858	1724	10727	930	910	30	32	56.8	28.0	7.0	3.0	5.2	I+II	Raw naphtha Injection to the common Hydro-carbon Header Started on 14.7.71 at 9.40 P.M. @ 150 Kg/Hr
	26.7.71	5600	3922	800	,,	1833	1694	10922	930	850	35	36	57.2	26.6	8.0	2.8	5.4	I+II	
	31.7.71	8000	3955	800	,,	1965	1717	11886	955	825	35	32	57.0	26.4	7.6	3.2	5.8	I+II	
	24.9.71	N.A.	4417	830	,,	1462	1880	11452	890	865	20	32	57.6	26.8	7.3	3.3	5.0	I+II	
	7.1.72	N.A.	4020	800	,,	1830	1394	9024	925	795	20	30	56.4	26.6	8.0	3.4	5.6	I+II	
	30.4.72	5437	2070	400	,,	830	801	5726	—	780	—	30	57.4	26.0	7.6	3.0	6.0	II	
	25.9.72	6166	2630	495	,,	1075	1054	6701	—	830	—	58	28.6	28.6	6.6	3.2	5.4	II	
V	4.11.72	5850	1840	900	Raw Vapour	1177	1105	5991	—	800	—	62	57.0	32.0	7.0	2.0	2.0	II	Raw Naphtha Injection with two new vertical vaporizers in line started in the morning shift on 4.11.72
	22.11.72	N.A	2045	1045	,,	1027	1045	8000	—	820	—	55	55.6	30.4	7.2	3.0	3.8	II	
	22.11.72	4200	3730	1175	,,	1702	1581	9561	925	830	25	40	56.2	28.0	8.8	3.0	4.0	I+II	
	23.11.72	4075	3530	1300	,,	1717	1846	10025	1020	835	23	42	56.3	28.2	8.6	3.3	3.6	I+II	
	29.11.72	N.A	3655	1325	,,	1972	2181	11813	865	810	28	55	56.4	28.2	8.2	3.0	4.2	I+II	
	30.11.72	N.A	4055	1366	,,	2067	2282	12355	865	800	30	56	56.0	29.4	7.6	3.4	3.6	I+II	
	7.12.72	N.A	3942	1375	,,	1939	2344	11777	870	810	28	50	55.6	28.6	9.0	3.6	3.2	I+II	
	10.12.72	N.A	3650	1393	,,	1997	2186	11795	845	810	30	55	54.6	29.2	8.8	3.6	3.8	I+II	
	18.12.72	4076	3697	1400	,,	1939	2203	12373	820	780	28	50	56.4	26.2	10.4	3.0	4.0	I+II	
	2.1.73	5800	3880	1425	,,	2133	2453	12716	850	815	30	58	55.4	27.0	8.6	4.4	4.6	I+II	

N.A.:—Figure not available

unit was locally fabricated and pressed into service in a very short time.

In the fourth phase of the experiment, vapour naphtha injection rates upto 800 kg/hr. were attained by running the new vertical vaporizer in parallel to earlier horizontal vaporizer from the scrap. As is clear from Table 1, the injection at the rate of 800 kg/hr. was continued for about one year and there was no sign of deterioration in the catalyst activity. Instead of effecting the performance of other units adversely, it displayed a stabilizing effect on the catalyst beds as well as on the cold boxes.

Considering the benefits realized in the fourth phase, another vertical vaporizer was installed which had almost the same capacity as the earlier one, in order to inject naphtha vapour to the maximum possible extent. Meanwhile, the hydrocarbon feed rate to the cracking unit reached the all-time low figure of 2400 Nm^3/hr. On the basis of our calculations and observations, a maximum injection rate of 1400 kg/hr. of naphtha with the available hydrocarbons and oxygen rates and without affecting the catalyst life was suggested.

The possibility of injecting naphtha alone was also ruled out because of the following reasons: (i) a major modification of cracking furnace as well as the naphtha preheater had to be carried out; (ii) the existing instruments and control system had to be replaced; and (iii) for the same capacity of hydrogen, both the shift conversion and carbon dioxide removal sections would be overloaded.

Though the injection rate beyond 1400 kg/hr. was theoretically possible, it was restricted within 1400 kg/hr. since due consideration had to be paid to factors, such as failure of the safety devices and availability of steam as well as oxygen. Nevertheless, the maximum rate of 1425 kg/hr was tried during the fifth phase of the experiment without encountering any significant problem.

Instrumentation : The important instruments installed for naphtha injection and also those already existing in the cracking unit have been shown in Fig. 4. The controller on the naphtha line ahead of vaporizers is a FRC A(L) instrument which can do the following jobs: (i) can control the flow as per its set point; (ii) can control naphtha flow to maintain a set value of naphtha-to-hydrocarbon flow ratio; (iii) will stop naphtha flow, whenever the unit trips; and (iv) will sound an alarm when the naphtha flow falls below 300 kg/hr.

In addition to the instruments shown (Fig. 4) there is

TABLE 2—Material Balance for Gas Reforming Plant

Case I: As planned by M/s Montecatini
Case II: Before implementing Naphtha Injection Scheme
Case III: After implementing Naphtha Injection Scheme

Stream No.	1			2			3			4			5			6			7			8			9		
Name of the Stream	Coke Oven Gas			Purified Coke Oven Gas			Raw Gas			Hydrocarbon Fraction			Cracked Gas Exit Cracking Sec.			Reformed Gas			Feed to Co-Shift Sec.			Converted Gas			Washed Gas		
Case / Composition	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
H_2	53.0	49.5	46.6	54.6	51.7	*	70.0	68.0	68.0	2.1	5.0	1.8	54.1	58.0	58.5	Not Applicable	65.0	65.2	54.1	60.0	61.0	62.4	65.6	66.6	82.0	83.0	85.0
CO	8.0	9.6	8.4	8.3	9.3		6.5	6.4	6.4	20.0	10.0	13.0	26.5	27.0	26.1		12.97	12.0	26.5	23.0	20.7	3.8	3.4	3.4	5.1	4.0	5.2
CO_2	3.0	4.8	4.6	—	—		—	—	—	—	—	—	7.3	7.0	9.0		15.48	14.8	7.3	8.5	10.9	23.9	23.6	23.2	—	—	—
CH_4	29.0	27.0	24.8	29.9	26.8		14.0	15.5	15.5	58.1	68.0	70.5	1.3	3.0	3.2		6.14	4.0	1.3	3.5	3.7	0.8	2.4	3.0	1.1	6.0	4.0
C_nH_m	3.0	3.0	2.0	3.1	3.0		1.3	1.3	0.7	5.7	5.0	5.1	—	—	—		—	—	—	—	—	—	—	—	—	—	—
N_2	4.0	5.6	13.2	4.1	8.6		8.2	8.3	8.9	14.1	11.4	9.1	10.8	5.0	3.2		0.41	4.0	10.8	5.0	3.7	9.1	5.0	3.8	11.8	7.0	5.8
O_2	—	0.5	0.4	—	0.6		—	0.5	0.5	—	0.6	0.5	—	—	—		—	—	—	—	—	—	—	—	—	—	—
Percent Total	100.0	100.0	100.0	100.0	100.0		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total Flow Rate Nm^3/Hr	11200	6000	5000	10771	5500		23861	19500	22000	5693	4000	3600	14631	9000	12000		5000	5000	14631	12000	12000	17821	19000	19000	13090	14000	14000

*Flow Rate and Analysis varies as per the Extent of Hydrocarbon Recycle one pressure gauge and one relief valve on steam side of each of the vaporizers.

Results

The experiment has proved very successful and boosted the production of ammonia by about 40-45 tonnes/day. Besides increasing production, it has stabilized the plant operating conditions in the following manner: (i) due to the fluctuation in the quantity and quality of coke oven gas, the composition of hydrocarbon fraction also fluctuates and sometimes, the hydrocarbon level in the separators of the cold box used to be so low that it allowed the leakage of hydrogen into the hydrocarbon fraction. This frequent slippage of hydrogen results in high hydrogen content and low calorific value of the hydrocarbon stream. The variation in calorific value from 4000 to 8000 Kcal/Nm^3 is clear from Table 1. With the present ratio control system, the oxygen flow is set as per the volumetric flow rate of hydrocarbons. The low calorific value gas for the same oxygen flow will result in high catalyst bed temperatures, flash back and fusion of the catalyst. Naphtha being a more concentrated fuel, its small volumetric flow will stabilize the calorific value of hydrocarbons, thereby making the catalyst bed temperatures and the cracked gas analysis steady.

(ii) Previous to the naphtha injection, the raw gas feed to the gas fractionation unit contained coke oven gas and washed gas (from cracking and shift conversion circuit) in the approximate ratio of 1:1. Now, the cracked gas make is more as a result of naphtha injection. The coke oven gas supply also being reduced, the coke oven gas to washed gas ratio has become 1:3. Consequently, the effect of variation in coke oven gas composition is not pronounced in the overall mixture. The cold box gets a feed of almost steady composition and the temperature conditions in the box get stabilized.

(iii) All the units get fully loaded after introducing naphtha injection. This utilization of all the available capacity of the machines allows them to run efficiently, reducing specific consumptions.

All these improvements are clearly noticeable if Table 2 is read in conjunction with Fig. 5. The adoption of the naphtha injection scheme assumes all the more significance when it is realized that all these benefits have been achieved without making any additional investment.

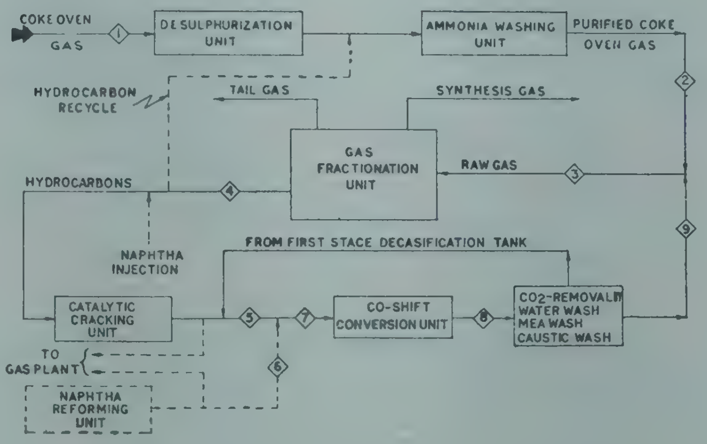
COKE OVEN GAS
1
DESULPHURIZATION UNIT
AMMONIA WASHING UNIT
PURIFIED COKE OVEN GAS
2
HYDROCARBON RECYCLE
TAIL GAS
SYNTHESIS GAS
GAS FRACTIONATION UNIT
RAW GAS
3
HYDROCARBONS
4
9
NAPHTHA INJECTION
FROM FIRST STACE DECASIFICATION TANK
CATALYTIC CRACKING UNIT
5
7
CO-SHIFT CONVERSION UNIT
8
CO2-REMOVAL WATER WASH MEA WASH CAUSTIC WASH
TO GAS PLANT
6
NAPHTHA REFORMING UNIT

Fig. 5—Block Diagram of the Gas Reformation Plant [Dotted blocks and lines are parts of supplementary gasification scheme]

Acknowledgements

The authors feel grateful to the General Manager, FCI Ltd. Sindri Unit for his continuous encouragement and support for carrying out such a risky experiment. The full cooperation extended by the production staff of Sindri Unit, particularly of Gas Reformation Plant, is also thankfully acknowledged.

(Original mss received on June 30, 1973)

UDC 66.065.55.013.5

Water Demineralization Plant Using Sindex—C26

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A 25 M^3/hr water demineralization plant has been designed and installed at the new pilot plant area of P and D Division at Sindri to meet the special requirement of water for the various process purposes such as production of catalysts, boiler feed, etc. In the plant, Sindex-C26* is used in combination with a commercial strong base anion-exchange resin De Acidite FF-IP, using a two-bed demineralizing process. The plant was commissioned and successfully run to produce the desired quality and quantity of treated water.

The plant consists mainly of the following equipments: two sand filters, one cation-exchanger vessel containing 3.3 M^3 of Sindex-C26, one degasser tower along with storage facility and one anion-exchanger vessel containing about 2.0 M^3 of De Acidite FF-IP. In addition, two numbers each of process water feed pumps, degassed water pumps and air blowers are provided.

For regeneration purpose, vessels have been provided for acid storage, acid measurement, acid dilution and caustic preparation. The diluted acid and alkali solutions are fed to the respective exchangers by means of water ejectors. The technical and operational data of the plant is given in Table 1.

TABLE 1—Operational Data

Details	Cation Exchanger	Anion-Exchanger
1. Normal capacity, M^3/hr.	25	25
2. Maximum capacity, M^3/hr.	27.5	27.5
3. Capacity between Regenerations, M^3	375	375
4. Resin (a) Type	Sindex-C26	Deacidite-FF
(b) Quantity	3.3 M^3	2.0 M^3
5. Size of Vessel		
(a) Diameter, mm.	1850	1570
(b) Height on straight, mm.	2100	2100
6. Quantity of Regenerant per regeneration	300 kg. H_2SO_4	100 kg NaOH
7. Regenerant solution concentration	2-4%	4%
8. Backwash flow rate, M^3/hr.Max.	40	20
9. Regenerant solution, flow rate M^3/hr. Max	15	10
10. Rinse flow rate		
(a) Initial	15	10
(b) Final	30	30
11. Total time for regeneration, min.	80-90	110

The process sequence is as follows: The process water is passed through the pressure filter with the help of raw water pumps. The filtered water is then passed through the cation-exchanger containing the resin Sindex-C26 in hydrogen form wherein the water is decationized. The effluent coming out through it is acidic in character containing the free mineral acids, the weak carbonic and silicic acids and a small leakage of sodium ions. Next the water is passed through the degasser tower to a height of about 20 ft. wherein air is blown from the bottom countercurrent to that of the water falling and this reduces the dissolved carbon dioxide content in the water to about 5-10 ppm. The water is then taken from degassed water storage tank with the help of degassed water pumps to the anion-exchanger containing the anion resin in the hydroxide form. Here the strongly and weakly base anions are exchanged resulting in the formation of pure demineralized water with a low conductivity.

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*a strong acid cation-exchanger resin, developed by the P and D Division, FCI Ltd.

When the conductivity of the treated water exceeds 15 micromhos/cm., the cation-and anion-exchangers are regenerated with 300 kg. of sulphuric acid and 100 kg. of caustic soda respectively. In order to minimize the precipitation of calcium sulphate in the cation-exchanger bed, half the quantity of the acid is fed as 2 per cent and the rest as 4 per cent. While the rinsing of the cation-exchanger is going on the anion resin is regenerated with 4 per cent caustic soda with the help of the decationized water stored in the degasser. Subsequently, the anion resin is rinsed to make it free from excess alkali and after the quality of the effluent water from the anion-exchanger is found acceptable, it is taken in line.

During the commercial utilization of the plant, its performance was found to be very satisfactory and the quality of the water produced on average is as indicated below (Table 2).

TABLE 2—QUALITY OF WATER

Inlet water	Outlet water
Total Alkalinity—100 ppm as $CaCO_3$	Total alkalinity—3 ppm as $CaCO_3$
Chloride—24 ppm as $CaCO_3$	Total hardness—Nil
Sulphate—80 ppm as $CaCO_3$	Silica—0.5 ppm as SiO_2
Total hardness—150 ppm as $CaCO_3$	Conductivity—5 micromhos/cm.
Silica—15 ppm as SiO_2	

(Original mss received on January 30, 1973)

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In the Indian Context

UDC 553.632:631.83

In the coming years the consumption of the potassic fertilizers will increase. In India there is not a single traditional potassic source of economic importance and thus the country has to depend upon imports. In this paper the available sources of potash and potassic salts and the processes for extracting them from insoluble silicates have been reviewed. It is possible to use to some extent the salt bitterns and brines apart from potash-bearing syenites and glauconites for extraction of potash as byproduct till a good marine evaporite having a high percentage of potash is discovered.

Availability of Potash from Non-Traditional Sources*

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In India a greater part of the projected increase in agricultural production has to be attained by intensification of agriculture, rather than by extension of cultivable lands. This can only be done by improved cultivation practices through optimum fertilizer application, as has been done in many countries of the world. For this purpose optimum balancing of the plant nutrients in successive application of fertilizers deserves a high priority. Of the three major fertilizer nutrients, viz. nitrogen, phosphorus and potassium, India is at the moment producing part of its requirements in respect of the first two only. There is no production whatsoever of potassic fertilizers mainly on account of raw material shortage. Potassic requirements are, therefore, met entirely by imports and consequently the optimum balancing of N:P:K for agricultural use is out of the question. It is, therefore, very necessary that to achieve the desired increase in agricultural productivity, the country has to locate exploitable deposits and sources—particularly land-based sources—of potash. Side by side, developmental efforts have to be directed towards working out new methods of potash recovery and manufacture of fertilizers from such discovered sources.

Conventional Sources of Potash

The bulk of world's demand for potassium is met from bedded deposits (evaporites) of soluble salts, mainly the chlorides and sulphates. Among the commercially exploitable deposits, the important minerals are carnallite (KCl, $MgCl_26H_2O$), sylvite (KCl), kainite (KCl, $MgSO_4$, $3H_2O$) and polyhalite (K_4SO_4 $MgSO_4$, $2CaSO_4$, $2H_2O$). Besides these, potassium-felspar ($K\,AlSi_3O_8$) and felspathoids, like leucite $K\ Al\ (SiO_3)_2$, glauconite ($KFeSi_2O_6$) (nH_2O) and muscovite $H_2\,K\,Al_3\,(SiO_4)_3$, are the important silicate minerals containing appreciable amounts of insoluble potassium. Another important insoluble potassium-bearing mineral is alunite, $KAl_6\,(OH)_2\,(SO_4)_4$.

Though reports are lacking on the large-scale exploitation and recovery of soluble salts from the above, the minerals containing insoluble potassium have been used only to a small extent.

India's Present Potash Position

So far not a single economically exploitable bedded potash deposit belonging to the evaporite facies has been reported in India. However, during the early part of this century and before the exploitation of Chile saltpetre, India used to meet the bulk of world's potassium nitrate requirements. Its output nowadays has become very much insignificant because of the poor quality of potassium nitrate or *reh.* At present its production—a few thousand tons—is restricted in the

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*Paper presented at the 60th session of the Indian Science Congress (Section on Geology and Geography), held at Chandigarh in January 3 to 9, 1973.

Gangetic districts of Bihar and U.P. and also in some parts of Tamil Nadu.

Though molasses, distillery wastes, waste woods and sea weeds are also known as sources of potassium carbonate, their production is too meagre to be worthy of any serious consideration.

Probable Sources

Sea based: Central Salt and Marine Chemicals Research Institute at Bhavnagar and The Fertilizer Corporation of India have done considerable work on the recovery of potassium salts from the bitterns[2,3] by solar evaporation of brine from sea water. It is estimated that any of this work, if implemented on a commercial footing, may yield around 75,000 tons of potassium sulphate per year.

It may be mentioned here that the world's largest production of potash salts from natural brines is obtained from the Dead Sea. The potash salts are recovered by fractional crystallization using solar heat. A similar process of recovery is now practised in many parts of USA, viz. Searles Lake, California, Bonnevilla and Utah.

Land based: No workable bedded potash deposits (evaporite) has so far been located in India. However, the environmental set-up favourable for the formation of potash deposit has been found to occur in several marine formations of the geologic past. For example, the occurrence of gypsum is fairly widespread in Rajasthan, Tamil Nadu, Jammu and Kashmir, Gujarat, and Himachal Pradesh. In these horizons, the precipitation of salts must have taken place due to evaporation as soon as the volume has been concentrated to one-half of the original bulk. According to Bateman,[4] gypsum or anhydrite is deposited when the volume reaches one-fifth, while the precipitation of common salt takes place at one-tenth of the volume. Below 0.0162 per cent of the bulk volume, the bitterns salts containing chlorides of potassium, magnesium and sodium and some magnesium sulphate yield different salts between night and day. The necessary concentration to induce precipitation of sea water by evaporation usually takes place in the submerged marine basins, along the margin of the continents, and separated from the main sea by the creation of some barriers, which do not allow the interchange of water from the open sea, as evaporation rate must exceed inflow of sea water to induce precipitation of salts.

India, with her vast coast line, shows existence of many natural cut-offs, in areas where sand bars isolate lagoons. Such cut-offs may also be formed as a result of delta building. Rann of Kutch in Gujarat is a classic example of natural salt pan.

Most of the salt deposits throughout the world consist only of calcium sulphate and common salt reflecting the incomplete evaporation of sea water. Yet the bondage between gypsum, rock salt and bittern salts is indisputable. Hence, it will be worth while to explore the possibilities of occurrence of potash salts in the gypsum and salt bearing areas of India. It is only the bedded potash deposits which alone can cater to the huge requirements of India to any significant extent.

Non-traditional Potash Resources: In many countries deficient in the conventional bedded deposit, insoluble potash used to be extracted out of silicate and non-silicate minerals. Thus, alunite, $K_2Al_6(OH)_{12}(SO_4)_4$ in Bulladealah in New Castle (Australia) containing 5-10 per cent K_2O was commercially exploited.[5]

Leucite, containing 17-18 per cent potash (K_2O) and 22-23 per cent alumina, was enriched and the concentrate treated by a specially developed process—developed by Societa Italiana Potassa[6]—yielding alumina, silica and potash salt.

In USSR the nepheline syenite apatite rock in Kola peninsula (Siberia) is exploited to produce alumina together with alkalies and portland cement.[7] The recovery was possible because of the unusual nature of the rock, which after beneficiation for removal and recovery of apatite concentrate, yielded a 90-93 per cent nepheline concentrate analyzing (per cent by weight) approximately as follows: alumina 29.5, silica 43.5, ferric oxide 3.5, sodium oxide (Na_2O) and potash (K_2O) 7.8. The by-products obtained per tonne of alumina produced are soda ash 0.62—0.76 t, potassium carbonate 0.18—0.28 t and portland cement 9.0—11.0 t.

In South Korea, a highly citric-soluble potash fertilizer was obtained by calcining a mixture of limestone and potassium-felspar, the optimum conditions being as follows: temperature 1250°C, time 10 min., particle size—200 mesh and CaO/SiO_2 ratio 0.8. A typical product contained 8.3 per cent potash (K_2O), 35.3 per cent lime and 42.3 per cent silica.

Glauconite has also been used in USSR as a source of potassium fertilizer[9,10]. The ore is pulverized to a fine powder, mixed with suitable proportions of calcium chloride and calcium carbonate and heated to 1200-1300°C in a furnace. The potassium chloride dust was trapped for absorption while a suitable cement clinker forms at the bottom of the chamber.

Sanidine, containing 8.62 per cent potash K_2O, has been considered as a potential source of fertilizer raw material[11] in central Poland. In Japan potassium carbonate has been removed from dolerite[12].

In India, one process has been developed for the extraction of potash from Golconda potash feldspar[13] (K_2O 11.3 per cent). The mineral is heated with a mixture of some other materials at 800-900°C for 4 hours. The highest yield of water-soluble potassium or potash (91.8 per cent) was obtained in a 1:0. 75:3 wt. ratio mixture of felspar, calcium sulphate and carbonate following the formation of $CaSiO_3$, thus enabling production of potassium sulphate.

Though innumerable occurrences of felspar are known, its use has almost entirely been restricted to glass and ceramic industries (particularly the homogeneous potassium-felspar variety—non-perthitic). The felspars of commercial importance are obtained mostly from pegmatites associated with the granitic rocks. Quartz, the common associate, is removed by processing. The mining, upgrading, cleaning and the ready market for felspar in the glass and ceramic industry render its price prohibitive and as such anyone contemplating to use felspar as raw material for potash fertilizer is likely to find it uneconomical in India.

This prompted the present authors to consider the possibilities of the utilization of alkali syenites and glauconites, for which there is no dearth in India. Moreover, some of the existing processes for exploitation of insoluble potash as a by-product using the potash silicates as a starting material is also known, e.g. the process developed in the USSR.

The occurrence of alkali syenites has been reported from many parts of India, the notable among them are the nepheline syenite of Sivamalai in Tamil Nadu[14,15], nepheline syenite of Kishengarh in Rajasthan, Nepheline syenite of Mount Girnar in Gujarat[16], alkali syenite of Kunavaram in A.P[17] and alkali suites of Koraput in Orissa[18].

Recent systematic petrological study by Bose[14–18] has revealed that the average potash (K_2O) in the Indian nepheline syenite ranges between 6 and 8 per cent whereas the average total alkali ranges between 12 and 16 per cent. The average potassium oxide (K_2O) and total alkali percentage in the nepheline syenite as determined by Nockolds[19] are 4.34 and 9.34 per cent respectively.

The present authors recently collected some representative samples of alkali syenite from Yelagiri hills and Koratti (associated with carbonatite complex) in Tamil Nadu. The average potassium oxide (K_2O) and total alkali oxide contents in all these samples were around 7 and 15 per cent respectively.

A typical pink porphyritic alkali granite sample, collected near Talbhat in Jhansi district (U.P.) by the authors, was found to contain 7.08 and 11.13 per cent of potassium oxide (K_2O) and total alkali. The alumina content in almost all the nepheline syenites ranged between 20 and 22 per cent while in alkali syenite its percentage varied between 15 and 17.

It is seen from the chemical data that compositionally (K_2O, Na_2O and Al_2O_3) all the India syenite rocks closely resemble the Kola-nepheline syenite of USSR with less amount of alumina (29.5 per cent in Kola). The process developed in the USSR for nepheline is mainly aimed at the production of alumina for which shortage exists—along with the recovery of soda (Na_2CO_3) and potash (K_4CO_3) as by-products. In our context however, the situation is different, since India has no shortage of aluminium. However, this country has to find out suitable resources for potassium as it is difficult to foresee to what extent the same type of treatment for syenitic and alkali syenitic rocks will be commercially possible.

Glauconite occurs in many sedimentary rocks of India, among which the Vindhyan rocks of Mirzapur and Banda of UP and Kota of Rajasthan are noted for its abundance. It occurs in the form of rounded pellets as well as replacement of clay matrix of the lower Vindhyan sandstones. A detailed report on the mineralogy of the glauconite is being published elsewhere by the authors. Glauconite forms nearly 50 to 60 per cent by volume on an average of the sandstones from Banda area. The bulk analyses of the sandstone shows 3 to 4 per cent potassium oxide (K_2O) while separated fractions yield potassium oxide (K_2O) as high as 6 to 7 per cent. These glauconites have also been subjected to study for ultimate exploitation of portland cement with potassium oxide as a by-product. The thermal treatment and extraction of potassium salts from glauconites and alkali syenite is still under study.

Conclusion

The purpose of this review paper on the recovery of insoluble potash, as practised in many parts of the world, is to emphasize the importance of potassic minerals containing insoluble potash as a source, depending upon the country's requirement.

However, it must be understood that on the face of it, with huge proved bedded deposits of potash in the world and their large commercial exploitation, the extraction of insoluble potash in India by any of the known methods will not be economically viable unless the process concerned is backed by the returns on some valuable by-products. In any case, the issue requires extensive study.

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[Original mss. received on Feb. 20, 1973]

UDC 631.82:552.574

The author has made an economic analysis in the selection of feedstock in manufacturing nitrogenous fertilizers in the country, relying on a paper by Dr. S. K. Mukherjee and Shri S. K. Viswanathan of FCI Ltd. The price of fertilizers is very high and if profit element is considered, in all fairness it has to be pointed out that both the naphtha based and the heavy stock based plants have a commanding advantage over a coal-based plant both at present and up to 1975 considering all factors. The main argument for the coal based plant would be dependence on indigenous feedstock and immunizing an important production sector in the country, viz. agriculture, from international situation of imported petroleum. Coal-based fertilizer plants would save foreign exchange and expand employment opportunities in the country. Such fertilizer plants require a special support as regards ex-factory price if they are to compete in the market with petroleum based factories.

Coal-Based Fertilizers*

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This year there has been a serious shortage in availability of fertilizers for the agricultural programme. The scarcity has coincided with a serious drought in the *Kharif* period which has necessitated an all-out effort to increase the production during the rabi season taking advantage of favourable late rains. As a result of the fertilizer shortage, the production programme is bound to suffer. Fertilizer is the most important input, after water, for agriculture. If we are to be self-supporting in the various agricultural

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*Keynote address delivered at the FAI Seminar on *Fertilizers in India in the Seventies* held at New Delhi during Dec. 18-19, 1972 and published by kind permission of the author.

products required for our food and industrial economy and our export trade, we have to organise our fertilizer availability along with expanding our irrigation supports. The question has always been the quantum of fertilizers which is sufficient for a certain planned production. The National Commission on Agriculture went into the problem in some detail in their Interim Report on Fertilizers released in December last year and have pointed out how empirical and arbitrary are our assessments of requirements. The fact that the consumption was not rising as expected led to the extraordinary conclusion that we need not provide the fertilizer originally estimated as required for a certain production we wanted to achieve in the Plan period. The Commission has realised that the scientific base for evaluating the input-output ratio for fertilizers and crops under various conditions is not yet perfect. Within the knowledge available it was necessary for us to adjust the fertilizer requirement to the expected crop production and then work towards ensuring that this fertilizer is used by the farmers in their production programme. The Commission's Report mainly deals with the various steps necessary to streamline the distribution and meeting the demands of the farmer. The Commission has noticed a demand at one end and supplies at the other but a chaotic link between the two which failed to make both meet. The Fertilizer Association of India have taken up the work of estimating the requirement of fertilizers for the Fifth Plan period with a view to establishing the steps to be taken to produce the fertilizers. This exercise has been circulated at the end of October, 1972. The estimates are reasonable and should be worked for. Based on the trend line method the exercise has estimated that our requirements of fertilizers in 1978-79 will be nitrogen 5.104 million tonnes, P_2O_5 1.924 million tonnes and K_2O 0.919 million tonnes. The Ministry of Agriculture, on the advice of the National Commission on Agriculture, has formed a Study Group to estimate scientifically the fertilizer required for the production envisaged during the Fifth Plan period. The figures given in the exercise of the Fertilizer Association can be updated when the Study Group's conclusions are available.

This article is being limited to the nitrogen availability. The study of the Fertilizer Association has calculated that the factories that are now in operation, the projects under implementation and expected to be on stream in the Fifth Plan and the projects likely to be firmed up by the end of the Fifth Plan will have an effective capacity of 4.4 million tonnes of nitrogen by April 1979. On the expectation that in the first year of commercial production the performance will be 35 per cent and in the second year 75 per cent rising to 80 per cent thereafter, it has also been worked out that normally this capacity should give an actual production level of 3.474 million tonnes leaving a gap of nearly a million tonnes by April 1979. As completion of a project, from the order to go ahead to production, takes anything from 3 to 5 years, if we are to make up this gap within the Fifth Plan period, it is now necessary to take our decisions. The study has recommended that at least 12 factories of a capacity of 2 lakh tonnes each of nitrogen should be planned and ordered immediately to bridge the gap in the indigenous availability of nitrogen by 1978-79. For our discussions we may take this as a broad objective.

The main problem we are going to face in ordering for future nitrogen plants is the selection of feedstock. The feedstocks can be natural gas, naphtha, liquid ammonia, heavy stock and coal. Electricity has been used in Nangal, but we are aware of the difficulties of getting electricity as a feedstock at a sufficiently cheap price. We may, therefore, not think about this, We have planned the fertilizer plants in operation, in stream and expected to be on stream in the Fifth Plan on natural gas, naphtha, liquid ammonia, heavy stock and coal. The time has come to dispassionately assess the situation of the continued supply of feedstocks for the ever-expanding programme of nitrogen fertilizers in the country and plan our strategy for the 12 new factories so that we are not caught by surprise by the world forces in petroleum markets.

The demand for crude oil in our economy for our various needs of petroleum products and also fertilizers is far in excess of the crude oil that we can extract from our own oil wells in the country. These oil wells also appear to be gradually reducing their output and we have not been able so far to establish any large new fields which can stabilize our crude supply for the next 30 years and also increase the supply to meet anything like our expanding demands. We all know how the world has been held to ransom almost every year by the countries who have been fortunate enough to have been endowed by nature with large sources of crude oil. At one time it was thought that the discoveries of large sources of natural gas in new areas may act as a deterrent to this tendency but logistics of natural gas transport over long distances and the new investments that are needed are not yet quite clear and we have yet to see how far these competing sources can steady the world crude oil market. We are, therefore, faced with the fact that today crude oil is a rising market and we do not know when the limits will be reached. The 1971 Tehran agreement has pushed up prices per barrel from $ 1.28 in 1971 to $ 2.05 in 1975. The present estimates are that there will be a further jerk up of 13.6 per cent over the 1975 level by 1978. The outlook is certainly not in favour of maintaining cost or stabilizing costs in crude. The price of naphtha, and the price of heavy stock must generally follow the price trend of crude. Naphtha has several industrial uses and we cannot expect any favourable adjustment for fertilizer production alone. There may be an argument that we can anyhow utilize a good part of heavy stock from our refineries to support the fertilizer programme. This again depends upon the pressures of the market and the availability of foreign exchange. We may have to crack our heavy stocks further to get fractions of diesel and kerosene to meet our essential demands for these commodities. Thereby, the fraction of heavy stocks left for both fuel oil and fertilizer production may be reduced. The liquid ammonia market is linked up with the natural gas market and as we have already realised, the future tendency is not clear. The competitiveness of natural gas sources against crude oil sources has yet to be established. It is against this background that the possibility of basing a good part of our future fertilizer programmes on coal as feedstock can be considered.

Coal transport for long distances is costly. Handling is also expensive. The present view, therefore, is that the fertilizer complex must be located almost on the mines so that the coal moves by conveyor straight from the mine to the factory, therby reducing handling and transport costs. The coal has to be of a fairly uniform quality as regards its various constituents and the dust content in gasification and as such large seams of uniform quality will be required to support the fertilizer plant for a 30-year period. This will further restrict the centres where the plants can be located. At present, three centres have been identified where large seams are available and the coal is considered suitable. These are Talcher, Korba and Ramagundam. All these three coalfields can possibly support several more fertilizer plants if need be. The Talcher quality can be struck again at Hingir-Rampur near Jharsuguda in Sambalpur. The Singrauli belt which now feeds the Obra Thermal station may be a possible source. This needs investigation; so also the Singareni and other deposits nearby. The study of the Fertilizer Association shows that by 1978-79 the northern zone will be deficient by a million tonnes of nitrogen and the southern by 0.684 million tonnes. The central zone will be deficient by 0.2 million tonnes. Ramagundam expansion may be able to look after the central demand. To meet the northern deficits from Korba or, say, the Singrauli belt, it may be necessary to bear an initial additional transport charge over 400 miles compared to plants that may be located in this zone. Similarly, 400 miles help to Talcher and much less for Singareni will bring the fertilizer near Vijaywada and this should enable a fair mobility in the southern zone. If this cushion can be built into the system, theoretically there is no difficulty in planning our coal-based fertilizers on these known coal seams. The present transport rates for fertilizers over 400 miles on the railway is Rs. 40 per tonne. If this advantage can be given to the coal-based fertilizer plants they should be able to compete with the other fertilizer plants provided the cost of production compares.

At the Second International Fertilizer Symposium at Kiev (USSR), held in September 1971, Dr. S. K. Mukherjee and Shri K. S. Viswanathan presented a paper[1] on Ammonia production based on various raw materials. I am relying on this paper and the up-dating of the calculations further by Dr. Mukherjee for the economic analysis. In that paper a comparative study has been made of five fertilizer plants to produce ammonia, in stream or to go on stream in the country. One plant is based on natural gas, two on naphtha, one on heavy stock and one on suspension gasification of powdered coal with oxygen. The detailed particulars of the five plants (A), (B), (C), (D) and (E) are given at Appendix 1. Table 1 gives the relative investments on the five plants.

TABLE 1—Relative Investment of Five Plants

	Investment per annual tonne of ammonia					
	Battery limits Plants cost			Total including facilities and financing charges		
	As per project estimate	Common basis		As per project estimate	Common basis	
		Rs.	R. 1.8*		Rs.	R. 1.8*
A	702	702	100	985	985	100
B	649	810	115	842	1,052	107
C	812	910	130	1,106	1.240	124
D	1,172	1,120	160	1,738	1,520	154
E	1,656	1,585	226	2,050	1,979	201

*Relative indices.

The actual estimates for the projects were made at different times and under different credit systems and fiscal policies and as such not strictly comparable. The authors of the paper, therefore, tried to work out the relative costs on a common basis. Plant (E) which is coal-based costs Rs. 1,979 per tonne of ammonia as compared to Rs. 1,052 in one naphtha-based plant (B) and Rs. 1,240 in another naphtha-based plant (C). Capital cost will no doubt be heavy. On the other hand, the foreign exchange outgo presents a different picture as shown in Table 2.

TABLE 2—FOREIGN EXCHANGE OUTGO, RS./TE AMMONIA

Feedstock	Feedstock Cost 1975, Rs.	Capital, Interest Repayment, Spares & Catalysts, Rs.	Total, Rs.
1. Coal (Indigenous)	—	128	128
2. Crude (Imported)	93	120	213
3. Heavy stock (Imported)	92	115	207
4. Naphtha (Imported)	230	133	263

As crude oil will anyhow have to be imported for all additional fertilizer plants, we have to compare the economics of an imported crude or naphtha plant *vis-a-vis* coal which is always indigenous. The permanent annual drain of foreign exchange for the import of feedstock is a heavy charge. This more than marks up the slight increase in foreign exchange in the capital cost of the coal based plant. There is tremendous saving in the total foreign exchange in a coal based plant. This country can tackle problems of internal finance for its industries but the greatest difficulty is in getting sufficient foreign exchange to support our industrial programmes. A foreign exchange saving proposition with no change in the end production is, therefore, most welcome. The extra capital investment in plant will all go in expanding our indigenous industries and expanding employment. From the objectives of our plan all this is welcome.

The cost of feedstock is an important element of the economics. Table 3 gives the feedstock requirements with their costs in 1971 and 1975 for the five plants under discussion.

The costs for petroleum based feedstocks have been computed on the basis of the price of the crude oil at $ 1.28 per barrel prevailing in January 1971. Recently, there had been an increase in crude price and it has generally been agreed that the same is to go up further. The feedstock costs in 1975 include an estimated increase due to the rise in the crude price to $ 2.05 by 1975. For coal the cost at Rs. 38.7 per tonne in 1971 has been assumed at Rs. 50 per tonne in 1975.

Based on the above feedstock requirements and costs and on the capital structure of the plants and the running costs including maintenance, labour, etc., the cost of production of the plants has been analysed in Table 4.

It will be seen that if the expected trends of petroleum and crude prices continue and coal prices also rise according to the general trend so far, in 1975 the relative cost of one tonne of ammonia produced from coal and one tonne produced from naphtha or heavy stock will be Rs. 496 and Rs. 450 respectively. In an urea plant where the ammonia stream is converted into urea in a continuing process, the parities of cost of urea to the ammonia is normally the same for bulk urea and bulk ammonia. If we add the bagging costs to urea for issue to the factory, a 20 per cent of bulk cost should normally look after the prevailing bagging prices. The allowance is on the liberal side. For the issue price of the fertilizers from the factory we have to add the profit margin. For our arrangements we may assume that the depreciation of plants having a relation to the capital involved, the profit element in the various factories will be equal to the depreciation factor in the cost per tonne. At present, there is a 15 per cent excise duty on the issue price from the factory and this will have to be added to judge the effect in 1975 on consumer prices. Table 5 gives the calculation of ex-factory issue price inclusive of excise and profit for the five plants.

TABLE 3—FEEDSTOCK REQUIREMENTS WITH THEIR COST IN 1971 AND 1975 FOR THE FIVE PLANTS

Plant	Feedstock	Feedstock Requirement, KCal/Te^{6}NH$_3\times 10$	Cost in 1971		Probable Cost in 1975	
			Rs./10^6 KCal	Rs./Te NH$_3$	Rs. 10^6 KCal	Rs./te NH$_3$
A	Natural gas	9.95	15.1	150	22.6	225
B	Naphtha (reciprocating)	8.50	20.46	173	27.4	232
C	Naphtha (centrifugal)	10.45	15.6	163	21.9	229
D	Heavy stocks	8.20	13.4	110	18.8	152
E	Coal	11.10	6.9	77	8 6	95

TABLE 4—COST OF PRODUCTION FOR THE PLANTS A, B, C, D & E, RS./TE NH_3

Cost Element		Plants				
		A	B	C	D	E
1. Feedstock	1971	150	173	163	110	77
	1975	225	223	230	152	99
2. Utilities	1971	9	38	14	46	71
	1975	9	38	14	53	80
3. Consumables and maintenance materials		45	79	51	57	76
4. Labour and overheads		10	11	11	11	13
5. Insurance, local taxes, general expenses, interest on working capital and contingency		20	27	20	25	30
6. Credit for steam		—	34	—	—	—
7. Cost of production before depreciation and interest	1971	234	294	259	249	267
	1975	309	344	325	298	298
8. Depreciation		99	105	124	152	198
9. Cost of production after adjusting depreciation and interest	1971	333	399	383	401	465
	1975	408	449	450	450	496

TABLE 5—EX-FACTORY ISSUE PRICE INCLUSIVE OF EXCISE AND PROFIT FOR THE FIVE PLANTS

Particulars		Plants				
		A	B	C	D	E
1. Cost of production of ammonia after adjusting depreciation and interest-wide item 9 in Table 4	1975	408	449	450	450	496
2. Cost of urea-Item 1+20 per cent		490	539	540	540	595
3. Profit equal to item 8 in Table 4		99	105	124	152	198
4. Assumed issue price at factory of urea		589	644	662	692	793

These final figures of issue price have not got the accuracy of cost analysis which upto the stage of cost production after adjusting the depreciation and interest has been worked out by Dr. S. K. Mukherjee in Table 4, for the five plants. I must make this clear; but the final magnitudes are sufficient for the purpose of the arguments I am raising.

The price of petroleum in 1975 has been assumed on the basis of the Tehran Agreement of 1971. Since then there have been two further agreements whose effect on the future petroleum prices is not yet clear. The consumer who is at the receiving end of all these rises can safely assume that the further two conferences were certainly not to give him any benefit but rather to mulct him further to the extent possible. The general judgement about energy stocks in the world in the form of petroleum is that there will be pressure on stocks during the next decade and further. This also points to rise in prices. On the other hand, in all fairness it has to be pointed out that both the Naphtha and the Heavy Stock plants have a commanding advantage on the profit element compared to a coal based plant and this difference has to be bridged in addition to the difference in the cost of production between petroleum based and coal based fertilizers of about Rs. 46 that will exist on the old calculation in 1975. We have also to take note of the extra transport charge of Rs. 40 per tonne in distributing the coal based fertilizer in the deficit zones in the North and the South. Petroleum prices will have to rise very high indeed before a naphtha or heavy stock based unit will be as costly as a coal based unit. The main argument, therefore, for the coal based plant would be dependence on indigenous feedstock and immunizing an important production sector in the country, viz. agriculture from the vagaries of international relations. There is also the large savings in foreign exchange in the annual import of petroleum feedstock. From this aspect, therefore, a certain percentage of our fertilizer production should be based on coal as feedstock as a safety measure. What this percentage should be is a matter of judgement.

I am suggesting that there is a case for another three plants at least immediately of a 2 lakh tonnes nitrogen capacity based on coal.

The country has already opted for three coal based plants of a capacity of 2 lakh tonnes of nitrogen per year. Two of them at Talcher and Ramagundam should be on stream by 1975. The third at Korba is being started very soon. These ventures of large-sized ammonia plants based on coal gasification are new in the world. The technology of coal gasification for ammonia production has been tried in smaller plants. The technological problems of gas composition seem to be quite within the competence of our technologists. The main problem appears to be the problem of dust in the gas. Filtering or removing the dust is the big technological problem which our scientists are expected to tackle and solve. These innovations in the technology can be normally expected with the scientific base that the country has already got. We are also being helped with the world knowledge in this matter. The innovation on technology, therefore, should not really deter us from embarking upon these projects.

The present pool delivery price of urea is Rs. 879 per tonne and this includes an average freight element of Rs. 40 per tonne. In addition to this, there is a distribution element of Rs. 80 per tonne of urea before the fertilizer reaches the farmer. Already prices are high and it is not desirable that prices should be increased further. As the factory issue prices have general relation to the pool basic price which would be Rs. 839 per tonne packed, we may for the sake of our discussions treat this as the price to be aimed at. If we deduct from this the excise that is at present levied, the ex-factory issue price cannot be more than Rs. 720 per tonne packed. The broad calculations in Table 5 show that whereas the petroleum based factories may remain just within this figure in 1975, the coal based plant will have to seek a higher ex-factory issue price if their production costs and profitability is to be maintained. Of course, if detailed cost analysis is done 1975 may be 1976 or 1977 or earlier. The main fact is that the coal based plant will require a special support as regards ex-factory price if it is to compete in the same market. Recently, in order to induce fertilizer producers to go for new plants based on Heavy Stocks, the Government of India have given special duty exemption for heavy feedstock. The obvious answer in the case of coal would be a suitable adjustment in the excise duty.

Incidentally, the present excise duty of 15 per cent is really making it impossible to cheapen nitrogen fertilizers to the farmers. If petroleum prices rise steeper than was anticipated in Dr. Mukherjee's paper[1], there will be a need to look into the duties on the fertilizers manufactured by petroleum based factories also. Anyhow, in the general interest of the agriculturists there appears to be a need to look into this aspect.

Summing up, I have tried to place a broad picture of the case for coal-based plants as was propounded by Dr. S. K. Mukherjee and his colleague in 1971 before a World Seminar. I would request that this Seminar gives serious thought to the problem from the aspect of national interests.

APPENDIX 1

Plant A: The plant is located near natural gas fields and natural gas is the feedstock for the reformer. The plant capacity is 910 tonnes per day and in single stream using centrifugal compressors. The plant is expected to be commissioned in mid-1974.

Plant B: An inland location and the feedstock naphtha is piped to the plant. The plant is in two streams using reciprocating compressors and is based on steam naphtha reforming. The capacity is 830 te/d ammonia. The plant is in operation for about one year.

Plant C: Is in a coastal location and is based on naphtha steam reformation. The plant uses centrifugal compressors and is in single stream. The capacity of the plant is 660 te/d ammonia. The plant is expected to be commissioned in mid-1973.

Plant D: Using partial oxidation of heavy stock is at a coastal location. The plant uses the single stream concept except for the gasifiers, which are in multiple units. Centrifugal compressors are used for all services. The capacity of the plant is 600 te/d ammonia. The plant is expected to be commissioned in 1975.

Plant E: Using suspension gasification of powdered coal with oxygen is located inland practically on the coal mine. The plant is single stream except for the multiple gasifiers. Gas/air compression is done in centrifugal compressors. The plant is expected to be commissioned in mid 1975.

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UDC 546.76:549.517:538.22

A ferromagnetic form of α-chromium sesquioxide is reported. It has a Curie point transition at 394°K, which is different from its Néel temperature (307°K). Structurally, the ferromagnetic form is indistinguishable from the antiferromagnetic form.

A Report on Ferromagnetism Observed in Chromium Sesquioxide

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Chromium sesquioxide, α Cr_2O_3 is antiferromagnetic[1], having a spin ordering of the corundum I type and a Néel temperature of 307°K. α-Fe_2O_3, another antiferromagnetic compound isomorphic with α-Cr_2O_3 exhibits a parasitic ferromagnetism arising from a canting of spins[2] of its corundum II type arrangement. The parasitic ferromagnetism disappears along with the antiferromagnetism at 893°K, showing that the same spin ordering mechanism is responsible for both. In case of chromium sesquioxide, however, the spins are aligned parallel or antiparallel to the trigonal symmetry axis and no nett magnetisation is observed. The present authors report here the detection of a weak ferromagnetism in α-Cr_2O_3 obtained by heating chromium trioxide.

Chromium sesquioxide is widely used as catalyst in a variety of reactions. It has been suggested[3] that its catalytic activity is correlated to its antiferromagnetic spin ordering. Any modification in that is expected to have important consequences.

Experimental and Results

BDH AnalaR grade chromium trioxide was heated in presence of air to different temperatures and durations. It was observed that prolonged heating at 400°C produced the most strongly magnetic α-Cr_2O_3 samples. At lower temperatures other oxides like Cr_2O_5, Cr_3O_8 etc. were retained, while at higher temperatures the ferromagnetism gradually disappeared to yield the ordinary antiferromagnetic form. Heating at 400°C for 5 hours produced a sample sufficiently magnetic to be attracted *en masse* by a hand magnet. Its magnetic properties were determined by a Faraday-type magnetic balance.[4] The observed parameters are listed below:

Curie temperature	: 394°K
Saturation magnetisation (extrapolated to 0°K)	: 1.2 C.G.S. units/g.
Effective Bohr magneton number	: 0.09
Colour	: Dark green, undergoing a distinct change on heating to just above Curie point, the change being reversible.

The room temperature ESR spectrum of the sample consisted of two lines. One of these is very broad and shows a large zero field splitting, so that the absorption maximum for that line could not be obtained in the record. The other line, at g = 1.98, having a half width of 1850 oersteds could be correlated to Cr (III) ions. The antiferromagnetic form did not show any absorption line below Néel temperature.

Explanation of the observed ferromagnetism in terms of departure from stoichiometry or retained ferromagnetic chromium dioxide phase was attempted. But on estimation of chromium to ±0.2 per cent accuracy, no departure from stiochiometry outside this error limit could be detected. The observed saturation magnetisation, if assumed to arise due to the presence of chromium dioxide, calls for a concentration of 4.5 per cent of that phase, which should be easily detectable by X-ray diffraction. However, the diffraction patterns of the ferromagnetic and the antiferromagnetic forms were identical in all respects.

Similar identity was observed also in the infra red absorption spectrum down to 250 cm^{-1}, thermogravimetric analysis curves and differential thermal analysis curves, except for a weak endothermic peak in the last named at 394°K for the ferromagnetic sample as may be expected at the Curie point. As far as structure is concerned, the two forms are therefore identical.

The observed ferromagnetism therefore must arise from a spin unbalance, and through a mechanism other than that responsible for the antiferromagnetic ordering. Had the two been the same, the ferromagnetism would have disappeared at the Néel temperature 307°K, as in haematite. Direct cation-cation exchange interaction has been established as the antiferromagnetic ordering mechanism.[5] Explanation of the observed phenomenon may lie in an enhanced cation-anion-cation interaction, which was shown by Osmond[6] to be of a ferromagnetic nature.

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[Original mss. received on June 28, 1973]

Technical Digests

A Process for Preparation of Active Magnesia for Removal of Silica from Water in Cold*

Magnesium oxide or caustic magnesia prepared by the conventional process of roasting raw magnesite at 800°-1000°C is generally used for various industrial purposes including desilicification of water along with hot lime or hot lime-soda softening process at a temperature around 95°C. Its use along with cold lime or lime-soda softening process does not give any effective silica removal at the ordinary temperatures.

In this patented process raw magnesite ($MgCO_3$–94 per cent minimum; SiO_2–4 per cent maximum) is crushed (to below 4″size) and roasted at a temperature of 500-800°C for a period of 30-120 minutes in a rotary furnace heated by gas or oil burners. The roasted mass is then cooled in air to room temperature and then ground to 40-200 mesh.

The active magnesia, thus prepared, is highly efficient in desilicification of water even when used along with cold lime or lime-soda process of water softening at ordinary temperatures. Silica of water can be reduced to a level of 1 mg./litre or below with a consumption of only 3-5 parts of active magnesia for each part of silica removed.

Triple Superphosphate at Sindri

On December 11, 1971, the then Governor of Bihar, Sri D. K. Barooah, laid the foundation stone of the Rs. 35 crores Rationalization Project of FCI Ltd. at Sindri. The main product from this project will be 3,46,000 te/yr of TSP and the others, 5,00,000 te/yr of by-product gypsum and 2,20,000 te/yr pyrites cinder.

The main plants for the production of triple superphosphate are sulphuric acid, phosphoric acid, TSP, material handling and bagging plants.

Sulphuric Acid: A 400 te/day plant has been set up by the Pyrites Phosphate and Chemicals Ltd. engineered by Simon-Carves which is now under operation.

The new 880 te/day plant, designed and engineered by Techno-Export Bulgaria, will cost Rs. 13 crores. Its process is as follows: Pyrites crushed into grains (0-6 mm.) with crushed elemental sulphur to the required sulphur concentration, will be fed to two fluidized bed roasting furnaces, where the temperature will be raised to about 900°C. At this temperature in presence of air, the pyrites will disintegrate into sulphur dioxide and purple colour pyrites cinder rich in iron. This reaction is exothermic and the liberated heat is sufficient to maintain the furnace temperature and the subsequent reactions.

Sulphur dioxide will contain a lot of dust particles which will be separated in a series of cyclones, electrostatic dust separators and washer after recovering the heat content of the gas stream for stream-raising. The clean cool gas will be heated again and sent through a converter for converting the gas to sulphur trioxide. This gas will be absorbed in sulphuric acid to produce 98 per cent acid. The utilization of the cinder in the production of steel is being explored.

Phosphoric Acid: This plant, having a capacity of 360 te/day of P_2O_5, has been designed and engineered by FACT Engineering & Design Organization (FEDO) in technical collaboration with Prayon of Belgium and is estimated to cost Rs. 7 crores. Imported rock phosphate ground to 200 mesh will be fed to a series of reaction tanks for treatment with sulphuric acid (conc.) to produce phosphoric acid and dihydrate gypsum. The slurry containing phosphoric acid will be centrifuged. The dilute acid after cleaning suspended solids will be concentrated in evaporators to 54 per cent acid.

The solids from the centrifuges will be reacted with steam and sulphuric acid to phosphoric acid. In this reaction dihydrate gypsum will be converted to hemi-hydrate and the resultant slurry will be filtered in Prayon filter to recover residual phosphoric acid which will be sent back to the cycle and the hemi-hydrate gypsum solids thus obtained from the filter will be slurried and will be utilized for production of ammonium sulphate in the existing plant in the Sindri factory.

Triple Superphosphate: This plant, designed and engineered by the Planning & Development Division, FCI Ltd., will cost Rs. 5 crores. Finely ground rock phosphate will be made to react with phosphoric acid

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* Ind. Pat. No. 107148 by G. S. Bhattacharyya, S. Singh, B. K. Dutta and K. R. Chakravorty, P and D Division, FCI Ltd.

(conc.) in large reaction vessels. The complete reaction being a very slow process the reacted mass will have to be stored in piles in a massive curing building. The cured lumps of TSP will be crushed, screened and packed. This project when implemented will save Rs. 9 crores foreign exchange annually.

Raw Materials: The consumption (te/yr) of raw materials will be as follows: pyrites 3,00,000, sulphur 75,000, rock phosphate 5,00,000, power 1,40,000 MWH and process water 2000 million gallons.

[From a Note Issued by Coordination Cell, Chemical Research Department, P&D Div., FCI Ltd., Sindri, June 30, 1973,]

Conferences, Symposia

Use of NPK Complex Fertilizers Based on Nitrophosphate Process

A symposium on the Use of NPK Complex Fertilizers Based on Nitrophosphate Process was organized by the Fertilizer Association of India during March 27 and 28, 1973 at New Delhi. Inaugurating the symposium, Sri A. P. Shinde, Union Minister of State for Agriculture, said that wheat production in the country could be doubled by the use of balanced fertilizers. With the introduction of the high-yielding varieties of crops the fertilizer (NPK) consumption increased to 27 lakh tonnes in 1971-72 from 7.84 in 1965-66. With the developments in fertilizer technology—which has striven to produce high analysis fertilizers—there has been a change in the pattern in the use of fertilizers. The use of high analysis complex fertilizers involves less cost in handling, transport, storage and application and being granular these fertilizers are easy to handle when applied to the soil. However, there is substantial imbalance in the consumption of NPK in India; in 1970-71 it was 6.3:2:1 against Japan's 1.4:1.1:1 and Belgium's 0.8:0.8:1. It was essential that efforts were made to improve the balance in the consumption of the 3 nutrients so that the lack of one nutrient did not become a limiting factor in obtaining the potential yields. In the areas growing high-yielding varieties of wheat and rice, widespread deficiency of zinc has been reported. Similarly sulphur deficiency for crops like groundnut and berseem has been noted. Modern fertilizer technology is striving at the production and use of ever higher analysis fertilizers, like ammonium polyphosphate (15:60:0), liquid mixed fertilizers, fertilizer suspensions and anhydrous ammonia. Micronutrients are also being incorporated in the fertilizers. The production of nitrophosphates has been drawing attention because its production and use can reduce or eliminate the use of sulphur which has to be imported.

In the keynote address, Sri S. Venkataraman of the Union Ministry of Petroleum and Chemicals stated that by the end of the Fourth Plan period, the ratio P_2O_5/N_2 would be only about 32 per cent as against the desirable minimum levels of 50 per cent and over. The programmes envisaged for the Fifth Five Year Plan anticipate an increase of phosphatic consumption from about 810,000 (in 1973-74), to 2.2 mil. tonnes by 1978-79, as a result of which the above ratio would improve from 32 to 42 per cent. However, the west zone has already achieved the desirable ratio of 50 per cent and the south zone 38 per cent in 1971-72.

For the production of 2.2 mil. tonnes of P_2O_5 by 1978-79, the requirement of sulphur would be around 2.2 mil. tonnes if the entire phosphatic production is in the form of ammonium phosphate utilizing sulphur for the production of sulphuric acid. Only about 10 per cent of the total P_4O_5 production may be based on sulphur resources, like smelter gas, pyrites and by-product sulphur, available within the country. The share of P_2O_5 based on nitrophosphate route is unlikely to exceed 14 per cent. Based on the current programmes, the production of about 2.0 mil. tonnes of P_2O_5 by 1978-79 would require import of about 1.4 mil. tonnes of sulphur involving an annual foreign exchange outflow of about Rs. 350 millions. If the sulphur required for imported phosphoric acid is to be taken into account the requirements will be even more. The production of 1 ton of P_2O_5 in the form of ammonium phosphates involves foreign exchange outflow for raw materials alone of over Rs. 750/te. At corresponding price levels the foreign exchange required for the import of phosphatic fertilizers amounts to around Rs. 1000/te. From foreign exchange saving considerations, the domestic production of phosphatics in the form of ammonium phosphates contributes only about Rs. 250/te of P_2O_5.

Dwelling on the impact of resources constraints on the fertilizers programme Sri Venkataraman stated that against the anticipated levels on consumption by 1978-79 of 5.2 mil. te of N and 2.2 mil. te of P_2O_5 the Approach Document of the Fifth Plan has considered the possibilities of domestic production limited to 3.912 mil.te of N and 1.174 mil. te of P_2O_5, based on which the ratio of P_2O_5 to N would only be about 30 per cent which is even lower than the current ratios. Against this background one has to consider alternatively the phosphatic fertilizers which eliminate totally or partially the use of sulphur, such as (1) use of by-products gypsum for sulphuric acid production, (2) use of hydrochloric acid for acidulation of rock phosphate and (3) the new process route for nitrophosphate production.

Due to the presence of impurities the use of the by-product gypsum has special difficulties which affect the property of the co-product, portland cement. The first commercial plant based on by-product gypsum has been commissioned recently in S. Africa. The development of a process in Israel using hydrochloric acid for phosphoric acid has created considerable interest which has yet to be commercialized due to corrosion problems involved.

In view of the above, the nitrophosphate process routes still offer the most attractive alternative for replacing the use of sulphur. Since the production of nitrophosphate requires, if at all, only marginal quantities of sulphur for balancing the grades, the foreign exchange savings out of domestic production are significantly high compared to ammonium phosphates. He cited the first attempt of nitrophosphate production in India at Trombay, the process route of which has been modified after trial to a product with 30 per cent of the total P_2O_5 in the water-soluble form. The Haldia fertilizer project includes facilities for production of nitrophosphate based on Stamicarbon sulphate recycle route. The Trombay expansion project also envisages production of 375,000 te/yr 20-20-0 grade of nitrophosphate.

The controversies on nitrophosphate have revolved round the following points: (1) production of suitable grades for basal application, (2) desirable level of water-solubility of the P_2O_5, (3) the efficiency of nitrate nitrogen in flooded paddy cultivation, and (4) the cost of import substitution in terms of additional rupee cost per unit of foreign exchange saved.

Working Sessions

Session 1: At the first session, which was presided over by Dr. J. S. Patel, Retired Agricultural Commissioner, Government of India and ex-Vice-Chancellor, Jawaharlal Nehru Krishi Vishwa Vidyalaya, Jabalpur, four papers were presented.

The paper[1] by J. Jung of W. Germany dealt with the utilization of phosphorus from NPK complex fertilizer based on nitrophosphate process and the leaching behaviour of their nitrogen components. He emphasized that in Europe a very large percentage of the total consumption of complex fertilizer was in the form of nitrophosphates. In preference to complete water solubility, the question of total phosphorus availability was now under consideration. There might still be disagreement about optimum ratio between the water and citrate soluble phosphate components in nitrophosphates. Jung established that monocalcium phosphate (MCP) and dicalcium phosphate were equally effective. He also emphasized that the greater part of the fertilizer phosphorus went to the soil phosphate pool and hardly 15 per cent was taken up by crops, the figure being 35 per cent of the grass land. Even in 10 years the utilization hardly exceeds 60 per cent and hence greater emphasis should be placed on residual effect while evaluating phosphate fertilizers.

Jung stressed that if nitrophosphates could be applied in a powder form, there was no necessity of any water-soluble phosphorus component but in case of drilling when granular form is used, a certain percentage of water solubility is desirable. In soil having pH between 5 and 7 there was difference between the WSP and CSP where used in powder form but when used in granulated form WSP is better than CSP. At higher pH, i.e. between 7 and 8, better responses could be obtained to a powder form, while in acid soils granular form would be better. In acid soils higher WSP was not desirable. According to Jung there was hardly any soil where plants survive 'hand to mouth' on the applied phosphate, as residual phosphorus was always available to the plant unless the soil was very low in phosphorus content, In neutral to alkaline soil 30 to 50 per cent WSP should be used as a safety factor. On the leaching behaviour of NO_3 and NH_4 nitrogen, distribution of rainfall and vegetation were the two most important factors. He emphasized that if the fertilizer application was tailored to the requirement based on crop growth stages, the nitrogen loss was negligible from the NO_3 component as compared to NH_4.

Presenting the next paper[2], I. C. Mahapatra gave the background of the previous work carried out in India on the efficiency of nitrophosphate which can be summarized as (1) response to phosphorus was generally higher with superphosphate, followed by ODDA nitrophosphate and least with the PEC nitrophosphate, (2) for long duration crops, like sugarcane, nitrophosphate was as good as superphosphate and (3) on acid laterite and sub-mountainous soils nitrophosphate gave as good (or even better) response as superphosphate but in alkaline or neutral soil nitrophosphate gave lower response.

He then presented results on the relative efficiency of nitrophosphate (having 30 N 50-53 per cent as WSB) as compared to a combined application of straight N and P fertilizers based on the experiments carried out during 1970-71 to 1971-72 under the All India Coordinated Agronomic Experiments Scheme which are as follows: (1) for **rice** (i) in 33 per cent of the centres on irrigated rice and at 3 centres under rain fed rice nitrophosphates (having 30 per cent as WSP) gave significantly lower response than AS+SSP, (ii) nitrophosphates with 50 to 53 per cent WSP was significantly inferior to AS+SSP only in 3 centres out of in 16 centres tested, (iii) Urea+SSP gave lower response than AS+SSP at 4 centres; (2) for **wheat** (i) in 2 centres out of 15, nitrophosphate with 30 per cent and 50-53 per cent WSP gave significantly lower response than AS+SSP. In 25 per cent cases nitrophosphate (30% WSP) gave higher percentage response of 100 and above, (ii) nitrophosphate with 50-53 per cent WSP recorded higher response of 100 or more in 5 out of 12 centres, whereas in the other centres the response to nitrophosphate was lower than AS+SSP; (3) for **jowar** (i) trials were conducted in 5 centres out of which in 2 centres the percentage response to nitrophosphate (30 per cent WSP) was lower than AS+SSP, (ii) in 4 out of 7 experiments with 50-53 per cent WSP nitrophosphate and in 2 out of 5 experiments with 50-53 per cent response was better than AS+SSP; (4) for **maize** (i) experiments conducted at 4 places out of which in two places no significant differences were obtained between nitrophosphate and AS+SSP, (ii) at Ludhiana the response with the former was higher while at Bhuvaneshwar the same was lower.

The pH of the soils, where inferior responses were obtained with nitrophosphate, varied between 6.5 and 8.2, which is in general agreement with the earlier data obtained. The higher response of AS+SSP might be due to the fact that the nitrophosphate contained nitrogen both in ammonium and nitrate forms unlike AS. The rice varieties gave different rating to nitrophosphate at one centre. Dr. Mahapatra indicated that the lower efficiency of urea+SSP as against AS+SSP could be due to volatilization and leading losses. If suitable techniques are adopted urea could be as effective as AS for rice.

The soils of Orissa, particularly red and lateritic, neither have a high phosphate status nor a low fixing capacity for phosphorus and the total sesquioxides and free oxides of iron and aluminium present in the soil create a favourable atmosphere for immobilization of applied water-soluble phosphates. In the third paper[3], N. Panda presented the results of experiments for testing water and citrate-soluble and citrate-insoluble materials for crops grown in laterite and red soils under pot culture. He stated that 70-80 per cent of the applied phosphorus in a water-soluble form got fixed in these soils and was not available to crops. Liming in these soils would have to be rapid every 2 to 3 years. According to him the partially acidulated rock phosphate with varying water- and citrate-solubility might be one of the means for minimizing phosphate fixation and to ensure an economic return from the application of phosphates. While comparing the relative efficiency of citrate-soluble sources like thomas slag and dicalcium phosphate with water-soluble source like SSP in red and lateritic acid soils of Orissa on maize, he concluded that partial acidulation of rock phosphate with a suitable amount of water- and citrate-soluble phosphate would be a suitable means for supplying the required amounts of phosphorus for plant growth. For acid soils, to provide some starter phosphate along with a potential source of 10-20 per cent acidulated material reasonable amounts of water- and citrate-soluble phosphorus would be suitable.

He also compared the effectiveness of different phosphate carriers for 3 crops of TN-1 paddy grown in pots. The results indicated that raw rock phosphate ground to pass 100 mesh was as good as 10 per cent acidulated material with phosphoric or nitric acid at lower level of phosphorus application. There was no significant difference in yield noticed among the treatments which received phosphoric or nitric acid acidulated products and also the corresponding mixture of rock phosphate and TSP at the corresponding levels.

A similar trend was observed with uptake of phosphorus. Partial acidulation either by addition of acid or mechanical mixture would be of equal value. A completely water-soluble phosphate source was not economical for acid soils.

In another experiment, Panda tried raw rock phosphate, Pelfos and TSP in a soil with 4-7 pH to study the residual effect. The cumulative dry matter yield and uptake of phosphorus of the 3 crops showed Pelfos to be an effective source containing almost all its phosphorus in citrate-soluble form.

Nitrophosphate not only provided a starter phosphate for early stages of growth of plant but also could be a potential source due to citrate-solubility for supplying phosphorus at the advance stages of plant growth. A large percentage of the cultivated land in eastern India is acidic and experimental data indicated that nitrophosphate containing lesser percentage of water-soluble phosphate would be an acceptable source. Quoting results of CRRI, Cuttack, he reported that good response had been obtained in rice with the addition of rock phosphate in low-land rice. With the introduction of multiple cropping system, the entire crop rotation was to be considered while evaluating any phosphatic fertilizer.

The last paper[4] in this session was by Prof. N. Atanasiu of Penang University, Malaysia, which dealt with the question of water-solubility versus citrate-solubility phosphate forms. There are numerous papers published recently, some of which indicate superiority of water-soluble phosphorus forms, while others that of the citrate-soluble phosphorus forms and finally a number of results showing equal effeciency. He summarized his field trial studies in the following: (i) For wheat, cotton and sugarbeet continuous need of phosphate and nitrogen could be observed during the whole vegetative growth period, which implied that soil must contain enough plant available phosphorus during the whole vegetative period, (2) crop plants were able to utilize equally both water- and citrate-soluble phosphate forms; they were also able to utilize lower soluble phosphate forms in which case higher phosphorus amounts were to be applied; (3) water- and citrate-soluble phosphate forms applied were being transformed after mixing with soil and in this mixture the water-solubility of MCP decreased at a high rate, while DCP showed comparatively a higher water-solubility; (4) pot and field trials demonstrate more or less an equal efficiency of MCP and DCP under different ecological conditions. DCP forms seem to have a wider range of efficiency since these forms can be better utilized by crop plants on both acid and alkaline soils; (5) some interactions between P-form and K-resp. Zn-nutritional state of the plants are reported.

Session 2: In the first paper[5] in this session, Prof. N. Atanasiu of the University of Penang, Malaysia stated that on the basis of his own results and those obtained in other countries in general both nitrate as well as ammoniacal forms could be equally effective. Ammonium fixation capacity of the soil was not an important factor in determining nitrogen response. Differences observed in the behaviour of ammonium and nitrate forms were large either over short periods of growth or in extremely different conditions.

In the next paper[6], S. P. Raychandhuri stated that both nitrate and ammonium ions are taken up by roots, but under agricultural conditions most of the nitrogen is taken up as nitrate because ammonium ion is converted to nitrate by micro-organisms in soils and also because nitrate is more mobile. Both the forms are equally effective except for flooded paddy especially as a basal dressing.

Broadly, the results of a large number of field experiments in India, UK, USA and other countries lead to the following conclusions: (1) For crops other than lowland and flooded paddy all forms of nitrogen are equally effective, except in the case of calcareous soils or for top dressing, or moderate doses of seed bed dressing for cereals when nitrite is more effective than ammonium ion. However, when large dressings of nitrogen are applied to seed beds or are concentrated near the seed, ammonium form is preferred, as nitrates are likely to adversely affect the growth of some crops; (2) for lowland or flooded paddy nitrates are not as effective as ammonium for preplant application because of high leaching and denitrification losses; however, at later stages of rice growth when the superficial roots are well established nitrate may be applied as top dressing. Efficiency of nitrate even for flooded paddy could be increased by increasing the number of split applications as the crop grows.

The management of added fertilizers in rice production has been a critical factor in determining the profitability in a given situation for rice production.

Session 3: In the first paper[7] in this session, the author, V. G. Vaidya, gave the results of a large number of trials both in experimental and farmers' fields in Gujarat, Maharashtra, A.P., Mysore, Tamil Nadu and Kerala which show that nitrophosphate is at par with other brands of fertilizer mixtures of urea, ammonium sulphate, superphosphate and complex fertilizers. The field trials have also indicated that it is not necessary to have all phosphate in water-soluble form and nitrophosphate containing 30 per cent WSP. The results further confirmed in pot culture experiments with different soils on paddy, *bajra* and wheat and applying nitrophosphate having different level of WSP tagged with P^{32}. There was no significant differences in yields from nitrophosphate either because of the nitrate nitrogen or of the partly water-soluble phosphate contained in this product.

He raised several basic questions some of which were (i) Is nitrophosphate, which contains both forms of nitrogen, as efficient as other straight and complex fertilizers containing only amide or ammoniacal nitrogen? (2) Is it necessary to have 30 per cent WSP in nitrophosphate for different crops and soils? (3) Is there a scope of maximising the yield by adjusting the departmentally recommended doses of NPK for various crops on the basis of soil testing? (4) Does split application of nitrophosphate give any advantage compared to one basal dose at the time of planting the crop?

In order to compare the efficiency of nitrophosphate with different types of complex fertilizers, straight and mixtures, V. G. Vaidya presented the results of triplicate trials on cultivators' fields where departmentally recommended doses of NPK were applied to sugarcane, potato, wheat, cotton, paddy and onion crops.

Nitrophosphate was also compared with other nitrogen carriers, viz. urea, ammonium sulphate, anhydrous ammonia and ammonia solution on paddy at various agricultural stations. Generally, there was no significant difference in the yield from different treatments.

The last paper[8] by John Omhalt, on experience with nitrophosphate in Pakistan, was based on experimental work carried out mostly in Punjab under irrigated conditions with the new high-yielding varieties of wheat, maize, rice and cotton in a large number of farmers' fields from 1967 onwards using different types of compound fertilizers and fertilizer combinations.

In general, complex fertilizers have given as good yield as the combination of straight fertilizers. Where the two types of nitrophosphates, viz. NP 20-20 and NP 23-23 have been compared the latter has given better yields. The difference in response is mostly caused by the effect of the water-solubility of phosphorus on this soil with high pH and low phosphorus status.

The other complex fertilizers, DAP and AP, have on an average given the same yield response as NP 23-23 though the latter in certain experiments had a tendency for better yields.

When potash was added, straight fertilizers and NPK 15-15-15 (from nitrophosphate) have had the same effect on yields. Generally, the data compiled indicate that under the predominant growing conditions of Pakistan highly water-soluble fertilizers are required.

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Science Research in India—Present Status, Factors Essential for the Proper Growth of the Same

Everybody agrees that all is not well with the scientific research and something somewhere has gone wrong. The research institutes which are supposed to be the seats of logical thinking, it is alleged, have degenerated into seats of illogical thinking. Those who are supposed to seek after truth, it is murmured, are after suppressing it. That the atmosphere in the laboratory is unconducive to research is an oft-discussed subject and many suggestions to improve it are made and nobody knows about its implementation. Yet another such discussion was organized by CSIR-Scientific Workers' Association of CFRI branch on 4th Feb. 1973 at the community hall of CFRI, Digwadih (Dhanbad). The presentation of 20 papers and attendance of more than 100 delegates to this seminar (which lacked official patronage) proved that conditions in the laboratories were far from satisfactory. The seminar was inaugurated and presided over by Dr. K. R. Bhattacharjee, President, CSIR, SWA.; Prof. K. R. Sharma, of Jadavpur University was the Chief Guest, while Shri S. R. Jagadish, President, CSIR-SWA CFRI branch was in the chair.

Dr. Bhattacharjee in his inaugural address spoke on the present status of the scientific research in India. He said that many of the present day ills in the laboratories, viz. mismanagement, favouritism and nepotism, publications of research papers/reports (where authorship is decided by seniority in posts and not by actual contributions) etc., were the outcome of the attitude of heirarchy and authority. Dr. Bhattacharjee said that the purpose of research is to bring social uplift; so industrial development and research should go hand in hand. He was particularly critical of the present system of seeking foreign collaboration, even on useless items, like manufacture of chicklets. He wanted to know who gained by these foreign collaborations—the country or the individual or a group of vested interests? He concluded by saying that science and scientific research in India would be meaningful only when the country sincerely wanted to be self-reliant in developing its own technology.

Prof. Sharma read out his paper analysing the state of research under CSIR laboratories during the past decades and the recent recommendations of the Sarkar Committee on the workings of CSIR. He pointed out that the expenditure on scientific research is negligible in relation to those in developed countries and there is almost no expenditure from private industries. Moreover, quality of research has been very poor and nothing has been achieved during the past decades. He specifically mentioned that science education in India had not been rationalized and there had not been any scientific manpower planning worth the name. In majority of the cases, foreign education is arranged on an individual basis, seeking higher degrees on subjects for which the country has no opening, resulting in loss of energy. He felt that the role of University in teaching/research should be recognised and basic research facilities should be provided in the university alone. The constraints, like restrictions on imported standard foreign equipment and chemicals, deterioration of general academic levels, career seeking students after entering higher posts (after their Ph.D.) losing all interests to learn new things, are reasons for general deterioration. One of the most important points he brought out about university education, was the danger of regional character being taken by most of the Indian universities which, he thought, they can ill-afford to be regional in character.

Then papers were presented one by one. The first paper 'Science and Service' dealt with the interdependence of man and science. Emphasis in that paper was laid on mathematics for development of science. In the second paper 'Role of Documentation in Development of Science' Sarbasri M. S. Deo and K. M. Sinha of P&D Division (FCI Ltd.) felt that documentation was one of the essential factors and prerequisites for proper growth of scientific research. They made an attempt to explain the utility of documentation in the growth of scientific research, and suggested various ways to solve the problems faced by research scientists in literature exploration.

In a paper on 'National Science Service & Research Centres' the author thought that one of the reasons for the slow progress of scientific research in our country is the lack of committed personnel including professors in scientific institutions. The author deplored that in spite of a large number of universities, a chain of research laboratories and other private research organizations, India has been able to produce only one Nobel Laureate in Science while a tiny country like Switzerland has 14. It has been suggested that the aptitude for scientific research should be inculcated at the earliest stage of education (i.e. much earlier to M.Sc. level). Sri S. R. Jagadish in his paper has traced the history of science in India and discussed the present status of science and technology with a focus on undesirable side effects. He has suggested enactment of an 'Indian Scientific Workers' Act' by Parliament.

Discussing the relationship between science and industry Dr. P. K. Ghosh of P&D Division pointed out in his paper that industrial research in our country is not sponsored by the users of the results of research. The reason is the virtual monopolistic status enjoyed by all industries in the context of huge demand. Only extensive industrialization of the country can bring forth the competition which will make industry aware of the value of research. Under that condition research will be both purposeful and remunerative, thus attracting better talents.

The next paper suggested that the method of morphological research may prove to be extremely helpful in improving the quality and quantity of scientific research in India. The problem of particle detectors in high energy physics was cited to illustrate the Morphological Box-Approach, showing that this method can help the inventions of four new types of particle detector.

Mr. C. S. Viraktamath thought that independent India had not got the proper return on what she had spent for the development of science and technology. The benefit of it has not reached the common man but, whatever it is, has gone to the elite. Improper National Science policy, stranglehold of foreign know-how, monopoly of business, etc. are among the many reasons for ineffective science and scientific research in our country. Remedial steps to make R&D effective, to reach the benefit to the common people and thereby to boost up self-reliance and national economy have been suggested. Mr. R. N. Bhattacharya in his paper expressed surprise at the rate at which management, marketing and sales were gaining importance over scientific research.

Scientific research has been recognized as an instrument for nation-building and socio-economic progress through self-reliance. The tradition of scientific research in India is very old as evident from Indian philosophy of *Naya* and *Vaisheshika*. The materialistic exploitation was rare largely due to ecological factors. In the last century the initiative for the development of scientific research in India was again lost due to untimely accent on heavy industries for which all the scientific know-how had to be imported. In the implementation of our plans for a short cut to prosperity the link between the research organisations and the needs and capacities of million of people of India could not be established. This is perhaps the major factor for the present static and confused state of scientific research, observed Sri B. R. Arora *et al* of P&D Division (FCI Ltd.). Still what the scientists in India have done is encouraging. Their achievements have started to create an impact on our society. But these achievements are mostly due to the efforts and sincerity of a few individual workers and not of a whole body of research organisations. The factors and the problems associated with the proper growth of research are of a very basic and fundamental nature. A brief discussion on these aspects formed a part of their paper 'Scientific Research in India —Historical Development, Present Status & the Factors Essential for Proper Growth'.

Need of a sincere approach was the theme of a paper submitted by Sri B. K. Banerjee of P&D Division. Growth of science is interrelated with the growth of national economy and social progress. 90 per cent of the R and D expenditure of our country is met by Government (Central & State) and provides employment to more than 90 per cent of the total scientists and technologists. It is quite natural to expect that if scientists make some positive contributions to the economy through their research endeavour, more and more attention would be paid by the Government to the growth of science. For a healthy growth of science, management bottlenecks should be removed, promotion rules should be rationalized and scientists should get recognition and incentives for their creative talents. As intellectuals, while scientists and technologists should not grumble for rewards, etc., management should also follow a uniform policy for incentives, taking account of the achievement, sincerity, economic impact and the like. Coordination and cooperation amongst different research organizations and amongst scientists and administrators, sincere and honest efforts by all sections of employees can bring about all-round development in the country as well as a healthy growth of science.

That failure in popularization of Science is one of the many factors responsible for the present unhappy state of affairs of Indian Science was the observation made by one of the authors. While discussing merits and demerits of media, viz. press, books, education, radio, TV and cinema, for the popularization of science, they stressed the removal of poverty andi lliteracy as one of the remedial measures.

Mr. G. G. Sarkar of CFRI in his paper thought that the following changes are essential in CSIR Laboratories. (i) Research activities should be oriented in such a way that scientific institutions may act as buffers between industry and universities. Although fundamental research should continue to be one of the major activities of national laboratories, greater emphasis should be progressively laid on industrial research including performance evaluation of plants and their technical audit on a periodic basis. (ii) Promotion in any scientific research organization should be done on a more rationalized basis in which adequate stress will have to be given on academic and professional qualification, seniority and experience of the worker as well as on the recommendation of the group leader under whom the individual works. (iii) Scientific workers should have a greater say in administration and project identification. A machinery has to be set up to counteract misrule/mismanagement of the organization and look into the genuine grievances as well as the welfare of the workers.

In a thought-provoking paper, 'Dilemma of a Young Scientist', Sri Kulkarni of P&D Division described the difficulties faced by a young Indian scientist in the age group 30 to 35, analysed the causes thereof and made an attempt to suggest some ways. Young scientists should develop the sense of social responsibility and keep in touch with the socio-economic condition of the country and should study carefully the techno-economic feasibility of the proposed research project. He was exhorted to be in constant touch with the library and to cultivate the reading habit. He was advised not to grumble about administrative delays since they are inherent in the organizational set-up. The vacuum created by the absence of a proper guide can be filled to a certain extent, by pen friendship with scientists working in other organizations on similar lines. The tendency of bossism can be curbed by introducing a system where subordinates should be consulted before promoting any scientist. Finally, the author concluded that all problems in the research organization are essentially human relations problems; so systems must be evolved to tackle individual workers imaginatively.

Sri A. N. Shriramalu *et al* classified research into four broad groups, viz. academic, applied, fundamental and industrial. The authors have gone in depth into the scope of scientific research in various disciplines, in detail into the petroleum industry and its R&D. The authors felt that in spite of the fact that India has as many scientists as U.K. or West Germany, it is but meagre compared to the size and population of the country. The qualitative achievements compared to the more advanced nations were also poor except for isolated cases. The authors preferred publication in Indian journals and felt that the craze for going into international journals should be discouraged. In their opinion this would raise the standard of the scientific journals published in India. They also recommend that the Annual Conferences of Scientific Bodies should call for quality articles for presentation. Such a get-together should also serve as a venue for discussion of scientific work and allied technical problems as a means of advancing knowledge. The handicaps of research in India are all common and due to lack of team work, inadequate facilities like documentation service, working materials, sophisticated instruments, trained technicians and above all bureaucratic procedures. The authors have suggested the remedial measures.

Sri Amarjyoti Basu suggested that people who execute plans and programmes should be given recognition and only efficient scientists should be entrusted with the responsibility of promoting research. Persons engaged in research should be kept free from the daily anxieties of making both ends meet. A strict vigil in different organizations should be maintained by a central body preferably having regional wings, so that no vested interests take root, no malpractice or nepotism creeps in and no stagnation of thoughts or activities creates a blockade in the way of rapid progress of meaningful research.

The afternoon session started with a brief summary of all presented papers by Sri B. K. Majumdar of CFRI. He commented that in all papers the underlying thought was: "What is wrong with Indian science in so many research institutes and universities?" He thought that the maladies and solutions suggested were not new; one had heard about them for the last decade and the only question is their proper implementation. After his resumé of the papers the session was thrown open for discussion. The initially languid discussion was converted into a lively one when delegates started questioning and cross-questioning. Mr. R. R. Rao (CFRI) thought that science and scientific research are not the same, and the common man does not care for science but is only interested in the result of research which can bring benefit to him. He thought that scientific research and industry should go hand in hand. About foreign aid, he thought that we may not import foreign technology but may seek foreign capital development. Shri J. Joga Rao (CFRI) thought that there has been a confusion between cause and effect and as a result there has been a set-back in scientific research. It is only by developing skill that we can be self-reliant and bring in self-sustained growth.

Dr. Guha Roy (CMRS) was of the opinion that education and science are in the hands of politicians and the old generation is reluctant to hand over responsibilities to the young people. This comment gave a turn to the discussions and young scientists poured out their grievances. Dr. M. Chakraborty (CFRI) thought that we did not lack sincerity but due to lack of inspiration from leaders, the young people did not work. He cited the examples of Sir J. C. Bose, C. V. Raman and Prof. S. N. Bose. Dr. C. S. B. Nair of (CFRI) commenting on the paper 'Dilemma of a Young Scientist' thought that most of the young scientists of today are not prepared to face hard work and they also lack sincerity. At this stage, Dr. Bhattacharjee asked why there was a crisis of character to which Dr. Nair replied by saying that insincerity was the root of all evils. Shri R. R. Rao pointed out that careerism in science only started after CSIR came into being and that has been the root of the dilemma of young or old scientists of today. In this context, he thought that CSIR-SWA may have a watchdog organisation to locate the areas and causes of frustation in young scientists and try to solve it.

Sri Kulkarni of P&D, the author of 'Dilemma of a Young Scientist', clarified that he did not try to put young against old or foster ill-feeling between junior and senior scientists. What he presented in his paper was an objective analysis of the situation.

Sri K. K. Roychaudhury of CFRI thought that most of the maladies of scientific research institutions in India had been due to the vastness of the laboratories, present employment situation in the country and lack of scientific spirit. Shri Ramalu (ISM) thought that it was not the degrees which made a good scientist but technical skill and intrinsic value of the person concerned. He also narrated certain obstructionist tactics of senior scientists in tackling scientific problems and publications. Shri J. Rao (CFRI) thought that it was the crisis of confidence rather than crisis of character that was standing in the way of proper growth of scientific atmosphere in the laboratory. He felt that the research guides must have all the resourcefulness of mind to provide the guidance and inspiration to juniors to carry out a project. Mr. Prasad of FCI felt that simply blaming seniors by juniors would not solve the problem. Young scientists should act in such a way that there was a change of mind in seniors.

Sri B. K. Majumdar (CFRI) thought that it was really the crisis of character, lack of sincerity and willingness to fight and stand against any evil deeds that were responsible for the present pathetic conditions of scientific research in India.

Dr. Bhattacharjee thought that early education and traditions imbibed in early youth might be responsible for making all of us ineffective. Here Sri Kulkarni of P&D commented that Indian culture was not conducive to scientific research, which was immediately challenged by many. Then Mr. Kulkarni explained that in research one always requires an inquisitive mind and should always ask the question why. But Indian tradition taught us not to ask questions to our elders. So the elders also never tolerate the questions from their juniors. In this atmosphere of submissiveness real scientific research is not possible. Dr. Tatke of FRI supported the view of Sri Kulkarni by quoting the example of Langmuir's theory of adsorption which was initially challenged by

Prof. Langmuir's own student Dr. H. S. Taylor, whereupon Prof. Langmuir did acknowledge the views of his student. He further posed a question to the audience, "Can it happen in an Indian University? If at all it happens, what will be the fate of that brilliant student?"

Shri B. K. Majumdar thought that the new philosophy of life, as embodied in unholy competition, racing after money, discarding of old values and deviating from the path of virtue, might be the reason for the complete deterioration in all spheres of our activity and society. Corruption has been a rule rather than exception.

Mr. S. Chowdhury (CFRI) raised the question—who actually gains by the corruption? If we can locate the same it will not be difficult to strike at the root but who represents the society today? Dr. A. K. Ghosh (CMRS) thought that a superficial structure which controls the Government is said to represent the society. Dr. C. K. Das (CFRI) thought that a particular section of the society, the so-called educated illiterates (?) who comprise hardly 25-30 per cent of the vast population, are said to be the society.

Sri Kulkarni (FCI) thought that a good piece of technology developed will always attract industrialists but in our laboratories only out-of-date processes/technologies are developed which find a natural death in the files. To this Dr. Bhattacharjee and others did not agree, they thought that our industrialists are always attracted by foreign technology—good or bad—for obvious reasons.

Shri A. C. Dutta (CFRI) asked whether it was possible to change the scientific research programmes' divorce from politics. Shri S. K. Banerjee of CMRS wondered why in large industrial ventures, e.g. restructuring of Jharia coalfields, Indian scientists were not consulted. He invited the scientists to join the forces which were trying to create a new society, free from nepotism and bureaucracy. On enquiry from a few scientists as to who comprise such forces Sri Supriya Chaudhury (CFRI) informed that it was the working/toiling masses of India who were fighting the evil forces of the superstructure of the society and scientists may join them to strengthen their hands.

Dr. C. K. Das (CFRI) spoke of the relation between education and dignity of labour; today education means learning to exploit the society, which he felt must change. Dr. A. K. Ghosh (CMRS) thought that the educated minority must be sympathetic to the vast majority of the people. He thought that if we wanted to benefit from scientific research, we must try to close the 'gap' between technology and social structure. Needs of 95 per cent of the population living in villages, their food, clothing, water, health, sanitation, etc. must be given proper weightage.

Shri A. C. Dutta (CFRI) referred to the present system of whimsical methods of project selection in the CSIR laboratories, for which the profit motives of the vested interests were responsible. A reign of anarchy existed. A system which can orient production for the masses can only bring about the much needed change.

Dr. Bhattacharjee in his concluding remarks thanked all the participants for initiating a very stimulating discussion. He compared the CSIR with a factory which existed only for itself without any social objectives. This inherent defect of a system is the breeding ground for the crisis of character. The scientists are doing research for their own benefits—their career, visits abroad, attending seminars at home and abroad and so on—and if this is the purpose of research, one can carry out research for centuries, but no benefit can ever accrue to the society. Such a closed aimless system can never bring any benefit to anybody. He listed maladies in scientific research and education as brought out in the seminar as follows: (i) quality of our research is very poor, (ii) universities are not well equipped to undertake industrial research programme, (iii) there is no proper transfer of laboratory research to industry, and industry of its own does not sponsor research projects. Solutions suggested in the seminar were (i) we should have competent scientists to guide research, (ii) red tapism must be stopped, (iii) good laboratory facilities be provided and scientists should be well looked after and (iv) better collaboration between research and industry should be ensured.

Book Reviews

An Introduction to the Properties of Engineering Materials by K. J. Pascoe (Published by Van Nostrand Reinhold Company, London), pp 394, price not stated.

The book is written with an idea of bettering the fundamental knowledge of material technology for the designers perpetually faced with the critical problem of the right selection of materials. It does not help him in his day-to-day work but improves his ability to adopt a better solution.

The way certain aspects, particularly of keen interest to a mechanical engineer, like heat treatment, alloying of elements, welding and fracture mechanics, have been dealt with calls for a remarkable skill and dexterity and enables the reader to achieve a lucid and comprehensive view of the processes involved.

The book also deals with elements of atomic theory of material and takes the reader step by step to the precipices built on the fundamentals. It would be equally interesting to any chemical engineer, specially the chapters dealing with equilibrium diagram, thermal energy and aggregation of atoms in different phases.

The illustrations and photographs in the book are much better than those found in common text-books and are arranged in such a way so as to help the reader in establishing in his mind a lasting impression which clearly indicates the immense efforts the author has taken in this regard to present the issues with such clarity.

This book would prove to be a good reference material for anybody who wants to have a better understanding of the problems in material technology.

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Soils of India (Published by the Fertilizer Association of India, New Delhi), 296 pages, Dec. 1972; Price Rs. 12.00

Soil is the key factor in agriculture. In order to achieve success in increased agricultural production, a thorough knowledge of soils and their management with respect to plant growth and nutrient uptake is of paramount importance. Hence, it is necessary to know the basic facts about our soils. Owing to the diversity of climate, geology, etc., there is a great variety of soils in this country and also greater complexity of problems.

The Fertilizer Association of India has recently published this book which comprises 23 chapters dealing in detail with soils of all the major States of India, except the Union Territories of Delhi, Goa, Tripura and Nagaland. The articles are written by the eminent soil scientists of India incorporating information on geographical location, physiography, climate, soil types found in the States, review of soil fertility surveys carried out in each State including the micronutrient status and crop responses to fertilizers in various agro-climatic and soil regions of the State concerned. In the case of Bihar soils, exhaustive information (in 5 chapters) on soils and their management has been given which is a complete scientific document so far the soil of an area is concerned. In fact, all these articles were previously published by the authors in the different issues of 'Fertilizer News'. Some authors have also added more up-to-date information especially on crop responses to fertilizer applications in various agro-climatic belts. FAI has done a good service in bringing these valuable publications in a book form for ready reference. The book will cater to a great extent to the needs of students, research workers and extension personnel in the field. Some authors have used 7th approximation system for classifying the soil types of the States, which will be extremely helpful to the students of pedology since most of the common text books lack such information about Indian soils.

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Rice by V. K. Sholapurkar and S. V. Balkundi, edited by T. M. Alexander (Fertilizer Association of India, New Delhi), October 1972. Pages VI+124, Price Rs. 5/-

This revised edition of the FAI booklet published in February 1969 written in a lucid, concise language contains up-to-date information on almost all the aspects of rice production in India, with particular reference to the progress made in the development of high-yielding varieties and suitable agronomic, water management, fertilizer use and plant protection practices for these varieties. It covers almost all aspects of rice culture, viz. (1) the main producing countries of the world including India with acreages and yields, (2) growth conditions, (3) species and varieties with emphasis on the details of high-yielding varieties, (4) various aspects of rice production technology starting from nursery raising to its harvest and cost of production, (5) manuring and fertilization, including response to micronutrients, fertilizer recommendation, national demonstrations and proper time and method of fertilizer application for economic return and (6) the future outlook of rice production.

In recent years a rapid progress is being made in developing new techniques in various aspects of rice production. The extension and promotional staff of various agencies, such as Directorates of Agriculture, fertilizer industries, manufacturers and distributors of seeds of high-yielding varieties, pesticides, agricultural machinery, commercial banks, etc. will find this booklet highly useful to equip themselves with the knowledge of the rapidly developing rice production technology and to bridge the information gap between the research workers on one hand and the farming community on the other. It will be valuable to students and research workers also as a source of useful information on the subject.

This booklet covers extensively the whole field of rice production technology, which is developing so rapidly that it is almost impossible to cite original literature in detail in a booklet of this size. However, the authors have given many useful references to important articles and books, wherever possible. It would have been more useful and attractive, specially to the field and promotional-cum-extension staff, by the addition of some illustrated, coloured photographs of the symptoms of important diseases and pests with their nature of damage, deficiencies and toxicities of the nutrient elements and the distinguishing morphological characteristics of the current high-yielding varieties for quick and easy identification. This book is strongly recommended to research, extension and promotional staff of various agencies actively engaged in stepping up rice production in this country.

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Key-Word-in-Context Index to Fertilizer Technology Abstracts

The Documentation Section of Planning & Development Division abstracts articles relating to fertilizer and allied technologies from various Indian and foreign journals received in its library and circulates them amongst the scientists and engineers of Fertilizer Corporation of India Ltd. This abstracting was started in 1963 as Fertilizer Technology Abstract (FTA) and till today contains more than 2000 entries. With more and more entries pouring in readers feel lost in a deluge of information. Understanding this difficulty of readers in information retrieval M/s M. S. Deo and K. M. Sinha have prepared key-word-in-context index to FTA.

This volume contains 1245 literature references taken from 128 various journals that appeared in bimonthly FTA. The period covered is from 1968 to 1972 and its 291 pages contains list of journal abstracted, title entries of articles along with citation and key-word-in-context index arranged alphabetically. This volume will help scientist, engineers or anybody to find information on any subject related to fertilizer technology. A few copies are available for free distribution and interested person may write to:

The Documentation officer,
P & D Division,
Fertilizer Corporation of India Ltd.,
Sindri (Bihar).

Notes & News

Recommendations of the Technology Transfer Seminar

The main recommendations and suggestions of the international seminar on technology transfer held at New Delhi in December 1972 are as follows:

(1) *Technology Transfer from Advanced to Developing Countries*: (i) **Acquisition of technology**—Import of technology by the developing countries is necessary to bridge the gap and accelerate socio-economic development. The buyers of technology from the developing countries are at a disadvantage in their bargaining position because of lack of technological infrastructure, of knowledge of different available technologies, etc. Such transfer cannot be treated purely as a commercial transaction between two parties. Institutional mechanisms at governmental level to supplement the market process are necessary. Every developing country set up a 'National Technology Corporation'; (ii) **Cost of Technology**—Measures are urgently called for to reduce the cost of purchase of technology by the developing countries, which should strive to have a common policy on science and technology where possible with the assistance of UN agencies, etc. UNIDO may explore possibilities of purchase of technology required by more than one developing country and selling it at subsidized rates to them consistent with their level of development; (iii) **Turn key jobs and package deals**—Technology transfer to the developing countries takes place largely through turn key jobs and package deals. This transfer should give much more information by way of how technology has been arrived at. The technological package involves the process/product know-how, design engineering, marketing, management and customer services, (iv) **Appropriate technology and selectivity in technology transfer**—Developing countries should develop the technological capability to select appropriate technologies and adapt and assimilate these for further development in accordance with their national needs; (v) **Policy on technology transfer and self reliance**—Each developing nation should formulate a comprehensive plan and policy on science and technology as an integral part of the national plans and programmes. Each nation should formulate its own socio-economic and technological plans for national development and priorities which should delineate areas where technology is to be developed locally and where import of technology is necessary; (vi) **Technological and management capability**—For effective absorption of technology the developing countries should establish adequate research and development base in the industries themselves. In the developing countries it may be necessary to create adequate scientific and technological infrastructure through universities, state sponsored industrial research and technological institutes, etc. (vii) **Institutional structure for transfer**—Appropriate institutional structure should be established in developing countries to monitor, regulate and give direction to technology transfer; (viii) **Central agency for technology transfer**—Each developing country would have to choose between the options of importing technology or generating it through its own efforts. It should set up an expert body to forecast technological sector-wise, level of technology to be imported or self-generated and priorities for indigenous research and development. UNIDO and UNCTAD should assist in making depth studies and surveys, intercountry comparison sector-wise and industry-wise to help the central agencies in developing countries, (ix) **Design engineering and consultancy services**—There is need to strengthen project engineering and design capability in the developing countries. This would lead to absorption and further diffusion of imported technology. (x) **Personnel policies and training programmes**—Technology is most effectively transferred by training scientists/engineers from the recipient countries on the shop floors of the developed countries. UNIDO and other UN agencies should organize specialized industrial training programmes; (xi) **Restrictive practices in technology**—International action through UN and other agencies is necessary to curb the activities of multinational corporations and international companies in enforcing restrictive practices in the developing countries; (xii) **Patent system**—where patents are purchased as a part of technology transfer by a developing country, they should include the rights to sub-licence these to other local industrial firms/developing countries for generating additional production; (xiii) **Trade names and trade marks**—Foreign brand names and trade marks should be permitted to be used in the manufactured products in developing countries; (xiv) **Economic and political aspects of technology transfer**—Technology transfer from developed to developing countries is not merely a commercial transaction but has economic and political aspects also. It should be left to purely commercial processes but should be integrated with the processes of socio-economic policies and plans of the governments. (xv) **Technology transfer as a global concept**—The world community as a whole should consider industrial and economic growth as a total system involving both developed and developing countries involving deployment of skills and labour force as world resources for overall global development; (xvi) **Role of international agencies in technology transfer**—International agencies, viz. UNIDO, UNCTAD and UNDP should assist in making depth studies of inter-country operation of technology transfer sector—and industry-wise.

(2) *Transfer of Technology between Developing Countries*: (i) **Information and data regarding technology transfer**—UNIDO should get up machinery to collect quantitative data in regard to technological transfer between developing countries. It may also publish information on such technology transfer: (ii) **Information regarding available technologies**—To generate and accelerate an interflow of technology between developing countries, each country must publish an inventory of information on technology available, including information specialized financing and investment agencies, banks, technology sale corporations and engineering consulting firms. UNIDO should take responsibility of bringing together these inventories—technology-wise and country-wise—to facilitiate technology transfer between developing countries in preference to technology transfer between developed and developing countries; (iii) **Special areas for techno-transfer**—Developing countries

have several agricultural commodities, marine resources and mineral wealth in common; technological experience in the field of common interest should be exchanged between themselves; (iv) **Semi-modern technology**—In the context of the situations obtaining in the developing countries, it may be necessary to make use of semi-modern technology in preference to sophisticated technology in certain circumstances. (v) **Selt-reliance and technology transfer between developing countries**—Availability of technology within the developing countries should help to lessen dependence on advanced countries and attain self-reliance. This would mean maximum utilization of indigenous resources including import substitution and development of technologies suited to the needs and factor endowments of the countries; (vi) **Sale of technology**—Developing countries should set up suitable agencies specifically designed to promote sale of technology, establishing direct links between the developing countries to accelerate technology transfer; (vii) **Identification of technological needs, cooperation and interregional arrangements**—Developing countries should set up organizations to identify their specific technological needs as also areas to which they can develop technology suited to their needs. A number of developing countries can join together and decide what they should import from developed countries; (viii) **Training of personnel**—Most of the developing countries do not have sufficient specialized institutional capacity for training personnel. Maximum use must be made of the available facilities and experience in developing countries, say by education and training of students in other countries, exchange of personnel and visits of delegations and exhibition; (ix) **Assurances and guarantees in technology transfer**—To overcome the distrust in the reliability of technology among developing countries, guarantees of performance could be given through clear demonstration of the actual industrial use of technology. Suppliers of technology must underwrite the investment and provide for penalties failures. Since the developing countries will not be able to afford loans and credits to other developing countries as a part of technology transfer process, international organizations like World Bank should place greater financial support for technologies available from developing countries; (x) **Selection of areas for specialized technology development**—Developing countries should coordinate their own plans to focus attention and efforts in specific areas of research and development and technology effort including engineering consultancy services so as to generate export potential for other developing countries. Technology transfer may take into account the socio-economic pattern of the recipient country and need not be a purely commercial transaction. Such transactions could be looked upon as cooperative system of industrial and technological growth where expertise may be assured from the developing countries. Some developing countries, which have the capability and the infrastructure to absorb imported technology from the developed countries and adapt it for their specific prevailing conditions, should be encouraged to make available such technologies to other countries. Schemes may be formulated for preferential treatment for transfer of technology between developing countries so that this may provide socio-economic benefits to the region on a bilateral arrangement basis; (xi) **Removal of restrictive practices**—International action could be taken to remove restrictive utilization clauses so that technology patented in or otherwise imported by the developing countries could be passed on by them to the other developing countries. When necessary, technologies in essential areas, e.g. population control, essential drugs and medicines, agro-chemicals, fertilizers, low cost housing and pollution control be acquired by UNIDO and supplied at nominal charge to the developing countries; (xii) **Publicity, communication links, seminars and conferences**—UNIDO might identify areas where technology transfer is necessary between different developing countries, publish success stories and failure cases and provide a forum for exchange of views of scientists and technologists.

(3) *Technology transfer for Laboratory to Industry*: (i) **R&D infrastructure in developing countries**—Steps must be taken to initiate industrial research and development in academic institutions and universities in countries, where a well-organized scientific and industrial research infrastructure has not yet been developed, when the availability of technologically trained personnel is limited, industrial companies should develop close liaison with research workers in the universities. Their research work should be oriented through frequent interaction with the operations of industry; (ii) **Personnel for industrial R&D**—Training of research and development personnel with right orientation for conduct of industrial research is essential. There should be a mobility between the research staff in the R&D organizations and the industrial firms/universities; (iii) **Planning for science and technology**—In the developing countries integration of the economic policies of the government with those for development of science and technology could lead to an accelerated transfer of technology from the R&D organizations to the stage of industrial production. There has also to be an inter-relationship between the policies for the import of technology and those of its indigenous development including absorption of acquired technologies and development of newer ones; (iv) **Identifying the problem and the user**—In most developing countries the first efforts in R and D would have to be in state sponsored organizations or universities. Systematic and close contact between R and D organizations, industrial users and the government is essential to determine the problem of relevance to industry and priorities for research and development and to ensure that the developed technology is exploited and used by the industry; (v) **Research management**—Resources invested in the establishment of and R and D infrastructure and facilities need a high degree of capability and expertize for production of optimum results. Attention should be paid even at an early stage in the developing countries to the training of personnel for management of industrial research; (vi) **Importance of development of, pilot and demostration units**—In most of the developing countries, marketing of results of indigenous research is possible only if it is carried out to the development stage to ensure for a degree of safety margin to the user. Adequate resources should be made available to R and D organization to put up pilot plant research and demonstration/prototype units; (vii) **Role of engineering consultants**—In order to ensure competent transfer, association of engineering consultants to design and engineer the plants based upon the know-how and technology developed by the research organizations is essential. The engineering consultant could then provide performance and other guarantees to the user; (viii) **Incentives for utilization of indigenous technology**—Industrial firms in the developing countries should be provided sufficient incentives if they have to be pursuaded to utilize the results of indigenous results in preference to import of technology; (ix) **Transfer of technology through personnel mobility**—There should be sufficient flexibility to permit a scientist/engineer to move out to the industrial firm for a limited period or permanently till the process has been successfully translated into industrial production; (x) **Role of a research development corporation**—For

effective transfer of results of laboratory results to industrial production, it is of advantage to have an agency like Research and Development Corporation which would have the responsibility to locate the right parties, negotiate terms, license the knowhow, arrange pilot plant demonstrations, contact engineering consultants and give rise guarantees; (xi) **Single-point transfer of technology**—It is essential that the R and D Corpr. or any other licensing agency is able to offer a package to the prospective entrepreneur; (xii) **Transfer of technology to rural areas**—The research and development and technology developed for rural areas should take into account the comparative backwardness of the rural community. The need for an on the spot demonstration, exhibition of a working unit and assistance in installation, erection and commissioning to create confidence in the rural areas is felt to a greater extent than in the case of urban areas; (xiii) **Language in technology transfer**—To ensure technology transfer within the rural and backward areas, special efforts should be made to produce technical literature in a language easily understood by the people.

[*CSIR News*, **23** (3) (1973), 17]

Beneficiation of Indian Phosphorite

India has reserves of phosphate rock to the tune of about 220 mil. tonnes but the majority of the deposits are below acid grade ($<$31.5 per cent P_2O_5) and high in the deleterious contents, like Fe_2O_3, Al_2O_3, MgO and free carbon, needing beneficiation. Rambabu and K. K. Majumdar of the Bhabha Atomic Research Centre have studied the beneficiation of the deposits at Mussourie, Maldeota (U.P.) and Kanpur (Rajasthan) and proposed processes for obtaining acid-grade concentrates.

Maldeota: One of our most potential sources, this sample (26:6 per cent P_2O_5) is most difficult to upgrade. The rock is hard and compact and contains carbonate, gangue, sericite, excess iron and pyrite both of which are intimately associated with cellophane. The rock was crushed and attrition ground in stages to-48 mesh 98 per cent and differential flotation techniques were employed. Fatty acid (Neofat 42-06 Armour Chem. Div.) was mixed with equal volumes of ethyl alcohol and light diesel oil and this emulsion was used as a collector both for calcite and cellophane. Sodium silicate was the gangue depressant.

Maldeota mined rock sample (17 per cent P_2O_5) was ground to −12 mesh 99 per cent and was calcined at controlled temperature 910°±10°C. After usual quenching and desliming the sands were further ground to about 60 mesh; the pulp was scrubbed and washed. Phosphate was floated out using R^3 mixture depressing quartz with sodium silicate or silicofluoride. The float was subjected to magnetic separation.

Kanpur (*Rajasthan*): The following calcination method for this sample (16.4 per cent P_2O_5) was developed: The rock was crushed to $-\frac{1}{4}$ inch size and calcined in a muffle furnace in batches of 0.5 kg at 960° ±10°C giving a retention time of 2 hours and the product while red hot quenched in fresh water. The white hydroxide in suspension is easily washed away. The resulting sands are remarkably enriched in P_2O_5 content.

Maton: The analysis (36.2 per cent P_2O_5) indicates that this is as such fit to be the acid-grade product. However, in the case of lower grade ore the same may be very easily upgraded by crushing, scrubbing or a little attrition grinding followed by washing for removing the cementing gangue. In the case of below 25 per cent P_2O_5 content samples flotation may be adoted to eliminate chert and grit.

Mussoorie: The ore (17.5 per cent P_2O_5) was crushed to 14/30, 30/60 and −60 mesh fractions. The two coarse fractions after thorough desliming were subjected to agglomeration tabling using an emulsion of fatty acid and sodium hydroxide. The fine fraction was subjected to oleic acid flotation using sodium silicate for depression of quartz and iron gangue. By this method acid grade concentrates assaying around 33.4 per cent P_2O_5 were obtained with an overall recovery of 74.7 per cent.

Another uraniferous sample (29.6 per cent P_2O_5) containing both carbonate and quartz gangue was ground to −48 mesh 98 per cent and heated at 500°C for 8 hours. Bulk flotation was then carried out with R^3 mixture (oleic acid, ethyl alcohol and diesel oil in 1:1:1 ratio) depressing quartz gangue with sodium silicate. The phosphate floats were cleaned by differentially floating out calcium gangue with the same mixture in starvation quantities maintaining slight acidity (pH 6), using monosodium phosphate plus gelatin as phosphate depressant. The tailing product (phosphate) after drying was subjected to magnetic separation to minimize iron content. This product ($-\frac{1}{4}$ in. size) was calcined at 900±10°C for 1.75 hours in a muffle and the calcine was quenched red hot in fresh water and deslimed. The washed sands with a little cleaning by magnetic separation could be turned into high acid grade concentrate.

[*NML Tech. J.*, **14** (2) (1972), 82]

Sixty Years of Science in India

There is certainly qualitative and quantitative improvement in science. Men like Srinivasa Ramanujan and C. V. Raman will always be remembered for their contribution to science. The place of science in tackling India's basic national problems was fully recognized and Indian Parliament adopted Scientific Policy Resolution during the tenure of late Sri Jawaharlal Nehru as Prime Minister. India's progress in producing fuel elements for atomic reactors, its growing aircraft industry all are examples of rapid progress. But though there was a further scope for all round progress in science and technology under strong political patronage science failed to achieve; that was the observation made by Dr. S. Bhagavantam in his presidential address to sixtieth (Diamond Jubilee) Session of Indian Science Congress at Chandigarh on Jan 3, 1973.

In his address he tried to review the progress of Indian science during last sixty years. Dr. Bhagavantham cited the example of Russia what it was forty to fifty years back. But to-day it has many firsts to her credit. And unfortunately to day he lamented that though there are great changes around us we continue to be there where we were forty years back, i.e. still in bullock-cart age. He remarked that our laboratories contain still a lot of imported equipments and in some instances instruments do not work at all. He observed that in our country research by industry or for industry, whether in private or public sector is at very early stage. And our investment both in funds and in manpower, in teaching and in research in the universities has been very much below par in relation to India's total scientific effort.

The speaker deplored our tendency to prefer to judge our capacities in isolation and not as the part of our contemporary world community. We are proud of our ancestors' achievements but this will not help to solve our present problems. Science and technology which generated the wealth in society was not equally distributed amongst all the members. So the author pointed out that majority die of starvation and minority of overeating.

There is always a pitfall in judging the contemporary work cautioned the speaker. The great discoveries are always accidental. They are never made at the demand of any body. Dicovery follows proper application. So progress in many cases could be retarded if assessment of such work is attempted during contemporary times. In developed countries the research is being carried out in different context. If we imitate that trend ihere we certainly will not be benefited. So a sound science policy is essential. We need a group of persons who are well versed in the art of decision making and who will lay down our priorities in science.

Talking of making plans to find employment for all the unemployable graduates is the example of putting the cart before the horse. The speaker could not understand the logic behind establishing scores of new universities while the already established ones are facing serious financial deficits and do not have facilities for technical education worth its name. He asked the audience how can educational standards be maintained with ill equipped laboratories? How can teachers who are drawn from amongst substandard degree holders contribute to inventive development and throw away imitative research? How can the leaders in science get right the ills that have crept into their programs, given such material to build their structures with?

He concluded his speech by saying that we certainly need to use science and technology for promoting our economic development. Our laboratories have to be modernised. Our libraries should endeavour to replace their stocks of obsolete books by more recent ones. Our teachers should bring themselves to be up-to-date by becoming students for a while. Our scientific programs should be looked at by someone who has a feel for their relevance and who is not so busy as those who actually handle them often are, and so on and so on. This is an unending chain and has irritating links in it.

KORBA FERTILIZER FACTORY

The foundation stone of the coal-based fertilizer factory at Korba, Madhya Pradesh, being set up by the Fertilizer Corporation of India Ltd., was laid on April 14, 1973 by the Prime Minister, Smt. Indira Gandhi.

The Rs. 120 crore Korba project, involving a foreign exchange component of Rs. 27 crores, would be completed in 42 months from the date the foreign exchange is released. The annual capacity of the plant would be 495,000 tonnes of urea.

The entire coal requirement of the project will be met by mines in nearby Surakachhar Colliery where the National Coal Development Corporation has invested Rs. 9 crores to build a production capacity of 1 million tonnes of coal per year.

The project planning, designing, engineering, procurement, construction supervision, commissioing and operation will be done by the Fertilizer Corporation of India. Licences and technical collaboration agreements with Koppers (West Germany) for coal gasification process and Montedison (Italy) for ammonia and urea processes have already been finalized by the Corporation.

News in Brief

Cotton Waste As a Soil Conditioner

Cotton waste, the waste product from ginning factories, is usually disposed of as such, or even occasionally composted along with other waste materials, and sometimes applied to field. Of late its application has become a regular practice in and around Coimbatore. Sri C. R. Laxminarasimhan *et al* of Soil Testing Laboratory, Coimbatore carried out an experiment in the black calcareous soils of Kallampalayam (Coimbatore Dist.) by growing a crop of Deccan maize in plots of five cents size with following treatments.

Treatment 1: 250 kg of 14:14:14 mixture basal and 50 kg of Urea as top dressing per acre (control)

2: Same as 1 plus 2 tons of cotton wastes per acre.

After the experiment it was found that soil pH and E.C. have been unaffected by treatment. There is a marked improvement in the physical properties of the soil due to cotton waste. The loss of nutrients especially nitrogen and phosphorus is more in the soil treated with cotton waste presumably because of the higher utilization of these nutrients caused by the incorporation of the cotton waste in the soil. This would have resulted in widening of the carbon-nitrogen ratio and more nutrients would have been utilized in the process of narrowing down of the ratio. The loss of nutrients due to the boost in the microbial population by the addition of the cotton waste can easily be compensated by advocating the additional dose of fertilizers.

The yield of grain obtained in cotton waste treated plant was 1,152 kg./acre and that from the control was 900 kg./acre giving an overall increase of 28 per cent due to treatment. The cotton waste used in the trial analysed for 1.52 per cent total nitrogen, 90.66 crude fibre and 15.49 per cent ash. Since as a result of the incorporation of cotton waste, an extra quantity of nitrogen has been added to the soil the yield increase in the grain is partly, attributable to this factor. As the analysis of the soil also show that the physical properties of the soil have considerably improved, this soil condition would have benefitted crop growth, and resulted in enhanced crop yield.

[*Current Science*, **42** (7) (1973), 245.]

National Information Service

In a report by an UNESCO expert, Mr. P. Lazar, the development of the INSDOC (Indian National Scientific Documentation Centre) as a coordinating national information centre to design a national information system for science and technology has been recommended. The report suggests that NIS should be based upon the existing information networks and services in the country and become an integrated national system. NIS should be planned and coordinated at the Government level by the National Committee on Science and Technology. The information systems for agriculture and on patents and other national information network in specific fields and disciplines be fitted into NIS, which should cover science and technology in their broadest sense, including information for industry, agriculture, medicine, public health and defence, etc. The report wants first priority to be assigned to the provision of information needed in the decision-making process at all levels of their activities including economic and financial, business and market information, information in the field of labour, sociology and other fields closely related to science and technology, to the application of research results and technical know-how.

The services to be provided by NIS should also extend beyond the limits of traditional library and information services, providing not only bibliographical information and specialized subject information according to traditional indexing and abstracting methods but also various types of evaluated and processed information in the form of surveys, state-of-the-art reports, progress reports, business and market surveys, other types of evaluated information, according to the needs of management on various levels. NIS has to arrange for data banks for the storage of numerical and other data in the field of physics, chemistry, other fundamental sciences, economics and statistics, making use of existing foreign and indigenous sources or extracting data from other information sources. NIS should be designed to accommodate both traditional methods of information handling and modern information technology based on highly developed reprographic equipment, telecommunication facilities and computers.

The report has endorsed the proposal of the Government to establish regional centres of information in Bombay, Calcutta, Hyderabad and Madras on the lines of regional centre established at Bangalore in 1964 facilitating access to the literature sources available in the region and to provide literature from outside the branch information centres and also local information units. Such units should be set up in every research and development institute, industrial firm and Government agency dealing with science and technology. It also gives the information that the INSDOC has prepared a complete plan and has taken up steps for setting up a national science library, which would have a cooperative acquisitive programme with the material relevant to the various national research laboratories themselves but integrated through a national union catalogue centrally situated and regionally disbursed through reprographic techniques.

Patents*

Stabilized Ammonium Nitrate Prills

M. L. Brown, A. W. Green, and E. L. Blanton (to Mississippi Chemical Corporation).

U.S. 3,630,712, Dec. 28, 1971, Appl. Mar. 12, 1969; 4 pp.

An earlier patent (U.S. 3,317,276, May 2, 1967) describes stabilizing NH_4NO_3 prills against the deleterious mechanical effects of crystalline phase transitions by incorporating H_3BO_3, $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$

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*These patents have been reproduced from Fertilizer Abstracts, published by the National Fertilizer Development Centre, TVA, Muscle Shoals, Alabama (USA) with kind permission of Editor FA —Editor into the prilling melt. The present patent specifies the optimum amounts and ratios of these additives. The H_3BO_3 is 0.125-0.135 per cent. The $(NH_4)_2 \cdot HPO_4$ is 0.15-0.2 per cent. The $(NH_4)_2SO_4$ is 0.0125-0.01 per cent. The ratio $(NH_4)_2HPO_4\ {}_2SO_4$ is 12-20:1. The ratio H_3BO_3:$(NH_4)_2SO_4$ is 10.13.5:1. And the ratio $(NH_4)_2$ HPO_4: H_3BO_3 is 1.2-1.5:1. A mixture of the additives is prepared by ammoniating a mixture of H_3PO_4 and H_2SO_4 then adding H_3BO_3 to the mixture and ammoniating further. (CF.S.African 69 07,070; FA 3,1877 and U.S. 3,418,255:FA 2,136).

[*Fertilizer Abstracts*, **5** (5) (1972), 105.]

Urea Synthesis

J. F. Villiers-Fisher and P. F. Kaupas (to Chemical Construction Corp.).

U.S. 3,636,106, Jan. 18, 1972, Appl. Sept. 12, 1968; 8 pp.

A process for high-pressure synthesis of urea is described in which recycle $NH_4NH_2CO_2$ solution is pressurized and stripped with feed CO_2 at, or slightly above, urea synthesis reactor pressure. The stripping step is carried out in a heat exchange zone, externally heated to decompose $NH_4NH_2CO_2$ and NH_3. The liquor from the stripping step is mainly water and can be discarded or processed to recover NH_3. Feed NH_3 is preferably added to the offgas to prepare a gas stream having a NH_3:CO_2 mole ratio of about 2:1. The gas stream is passed through a decomposer-heat exchange zone to heat the effluent from the urea synthesis reactor, thereby decomposing $NH_4NH_2CO_2$ in the effluent and producing an offgas which is processed to prepare aqueous $NH_4NH_2CO_2$ solution. In passing through the heat exchanger, the NH_3CO_2 gas stream is cooled so that $NH_4NH_2CO_2$ condenses. The resulting stream containing condensed $NH_4NH_2CO_2$ is fed to the urea synthesis step.

[*Fertilizer Abstract*, **5** (5) (1972), 105.]

Ammonium Sulfate-Ammonium Nitrate Fertilizer Pellets

A. L. Earl (to United States Steel Corp.).

U.S. 3,635,691, Jan. 18, 1972, Appl. Jan. 1, 1969; 5 pp.

Ammonium sulfate particles having a screen size of about 90 per cent 30+70 mesh (U.S. standard) and containing 0.3 per cent moisture are fed to a tilting rotating disc pelletizer. The $(NH_4)_2$ SO_4 particles in the pelletizer are sprayed with aqueous 80-90 per cent NH_4NO_3 solution at 250-300°F. The wt ratio $(NH_4)_2SO_4$:-NH_4NO_3 is no greater than 70:30, dry basis. Pellets of $-6+14$ mesh size, containing 4-6 per cent moisture, are discharged from the pelletizer. Products containing micronutrients can be prepared by adding a saturated solution of micronutrient salts to the NH_4NO_3 solution.

[*Fertilizer Abstracts*, **5** (5) (1972), 105.]

Phosphoric Acid Manufacture

A. C. Van Es and Arnoud Waller (to Albators Superfosfaat-fabrieken N.V.). U.S. 3,632,307, Jan. 4, 1972, Appl. Apr. 9, 1969; 9 pp.

In the hemihydrate-gypsum process for the manufacture of H_3PO_4 from phosphate rock and H_2SO_4 from phosphate rock and H_2SO_4 an improvement consists of washing the hemihydrate with aqueous solution containing 23-43 per cent H_2SO_4 and 1.8-7.5 per cent P_2O_5 as H_3PO_4. The washing is carried out under conditions which prevent conversion of the hemihydrate to gypsum. The washed hemihydrate is then converted to gypsum by recrystallization in an aqueous solution containing 1-15 per cent P_2O_5 as H_3PO_4 and 2-25 per cent H_2SO_4. The wash liquor from the hemihydrate washing step is recycled to acidulate phosphate rock. The filtrate from the gypsum filtration is recycled to the hemihydrate washing step. Cf. Neth. Appl. 6,612,150, Mar. 9, 1967: CA 67,34535.

[*Fertilizer Abstracts*, **5** (5) (1972), 106.]

Clarifying Phosphoric Acid

H. H. Naschke and R. L. Taylor (to Esso Research & Engineering Co). U.S. 3,644,091, Feb. 22, 1972, Appl. Mar. 17, 1970; 6 pp.

Suspended or dispersed solid impurities are removed from wet-process H_3PO_4 by adding 10-200 ppm of sulfonated polystyrene or its water-soluble salts having a molecular wt of 3-12 million. The additive can be introduced in the phosphate digestion step, in the H_3PO_4 concentration step, or in the concentrated H_3PO_4 prior to centrifuging to remove the solid impurities.

[*Fertilizer Abstracts*, **5** (5) (1972), 106.]

Removal of Fluorides from Phosphate Offgases

R. G. Hartig.

U.S. 3,642,438, Feb, 15, 1972, Appl. Apr. 15, 1969; 5 pp.

Combined waste gas streams from phosphate rock processing, containing HF,SiF_4, H_2O vapor, SO_2, and phosphate dusts, are prescrubbed with recirculated aqueous liquor containing SiO_2 and 25 per cent H_2SiF_6. The SiF_4 is not absorbed and leaves with the offgases. The HF reacts with the SiO_2, forming H_2SiF_6 which decomposes to SiF_4 vapor. The gases are then scrubbed with an aqueous slurry containing excess NaF which reacts with residual HF to precipitate $NaHF_2$ and with SiF_4 to precipitate Na_2SiF_6. The scrubber liquor is filtered, and the filter cake is dried and heated to 600 F. which decomposes the $NaHF_2$ to form NaF and gaseous HF which can be removed as product or recycled to the prescrubber. The solids, containing NaF and Na_2SiF_6. are then heated to 1300°F. whereby Na_2SiF_6 is decomposed to form NaF and gaseous SiF_4. The NaF is recycled to the scrubber liquor. The gases are scrubbed with water to prepare a solution containing H_2SiF_6 and precipitated SiO_2. is filtered off and a portion is recycled to the prescrubber liquor. The filtrate consists of a 15-25 per cent H_2SiF_6. solution which is removed as product. (Cf. U.S. 3,574,542: FA 4,1110)

[*Fertilizer Abstracts*, **5** (5) (1972), 107.]

Removal of Sludge-Forming Impurities from Phosphoric Acid

J. W. Kraus and C. C. Legal (to W. R. Grace & Co.)

U.S. 3,637,348, Jan. 25, 1972, Appl. Oct. 24, 1969; 4 pp.

Addition of 80-120 ppm of coal tar bases or acids to wet-process H_3PO_4 promotes flocculation and removal of impurities that form sludge during storage. For example, 100 ppm cresylic acid was added to freshly concentrated H_3PO_4 containing 55 per cent P_2O_5. The mixture was stirred for 18 hr at 70° and centrifuged. The sludge that formed during 15 days' storage was 27 per cent less than that from H_3PO_4 treated in the same way but without cresylic acid addition. Ethyl cresol or dimethyl pyridine can be substitute for cresylic acid.

Purifying Gypsum

J. T. Brent and J. S. Page (to W. R. Grace & Co.).

U.S. 3,642,456, Feb. 15, 1972, Appl. July 29, 1969; 4 pp.

Impure natural or byproduct gypsum is mixed with aqueous 15-26 per cent H_2SiF_6 at 160-195°F. whereby part of the $CaSO_4$ dissolves. The mixture is filtered at 160-195°F and the filtrate is cooled to 75-100°F. causing precipitation of $CaSO_4 \cdot 2H_2O$. The precipitate is filtered off, washed with water, and dried at 200-250°F. to produce gypsum of 99 per cent purity.

[*Fertilizer Abstracts*, **5** (5) (1972), 107.]

Converting Calcium Sulfate Hemihydrate to Gypsum

Hakuichi Akazawa et al (to Taki Fertilizer Manufacturing Co., Ltd.).

U.S. 3,645,677, Feb. 29, 1972, Appl. Japan Sept. 24, 1968; 8 pp.

In the manufacture of H_3PO_4 by treating phosphate rock with H_2SO_4 to prepare a solution containing H_3PO_4,H_2SO_4, and $CaSO_4$. 0.5 H_2O, followed by hydration of the $CaSO_4$. 0.5 H_2O to form $CaSO_42H_2O$, close control of operating conditions is required to produce the gypsum in the desirable form of short columnar macrocrystals. A method is described for insuring the production of gypsum in desirable form comprised of adding to the reaction mixture a surface active agent, for example. alkylbenzene sulfonic acid having 12 C atoms in the alkyl group. The beneficial effects of the agent are obtained only when the mole ratio H_2SO_4:H_3PO_4 is 0.5-5:1 and the total concentration of the mixed acids is 20-40 per cent. The amount of agent is 0.1-1.2 per cent, phosphate rock basis.

[*Fertilizer Abstracts*, **5** (5) (1972), 107.]

Granular Urea-Superphosphate Compositions for Use as Fertilizers and Feeds

P. I. Briggs (to African Explosives & Chemical Industries Ltd.).

South African 69 08645, Aug. 4, 1971, Appl. Dec. 23, 1970; 11 pp.

Urea-superphosphate mixtures normally become damp and sticky in storage because an adduct forms that releases water of crystallization from the superphosphate with molten urea and granulating the mixture by cooling to solidification in appropriate equipment; the water released is either vaporized or held within the granules.

[*Fertilizer Abstracts*, **5** (5) (1972), 109.]

Phosphoric Acid by Ion-Exchange Process

L. W. Cochran (to Multi-Minerals Ltd).
U.S. 3,645,682, Feb. 29, 1972, Appl. Sept. 13, 1967; 5 pp.

In producing H_3PO_4 from $Ca(H_2PO_4)_2$ by means of anion-exchange resin, an improvement consists of a 2-stage treatment. In the first stage, substantially dry $Ca(H_2PO_4)_2$ containing 10-14 per cent free H_3PO_4 is premixed with a substantially dry portion of the ion-exchange resin. The moisture content of the mixture is sufficient to promote migration of ions. In the second stage the mixture is contacted with the remainder of the ion-exchange resin. The method has advantages over a single-stage ion exchange treatment because $Ca(H_2PO_4)_2$ is not very soluble in water or H_3PO_4, requiring the passage of relatively large volumes of liquid through the resin bed.

[*Fertilizer Abstracts*, **5** (6) (1972), 136.]

Potassium Metaphosphate

J. W. Watson (to Swift & Co.).
U.S. 3,650,684, Mar. 21, 1972, Appl. Dec. 10, 1968; 4 pp.

The title product is made by reacting KCI with super-phosphoric acid in a free flowing bed of inert solids under essentially anhydrous conditions. For example, superphosphoric acid (71 per cent P_2O_5) was sprayed on a mixture of silica sand 11,350 and KCI 1268 g preheated to 260°, in a rotary drum. The acid was sprayed on to the rolling, cascading solids at a rate which maintained the temperature at about 260° until 1630 g had been added. When the evolution of HCI had stopped, an additional 1268 g of KCI was added, the mixture was preheated to 260°, and the cycle was repeated three times. The product contained 18.48 per cent available P_2O_5, 8.30 per cent water. soluble P_2O_5, 14.46 per cent water-soluble K_2O, 60.14 per cent SiO_2, and 3.38 per cent Cl.

[*Fertilizer Abstracts*, **5** (6) (1972), 138.]

Foliar Fertilizer Containing Carbon Dioxide

G. D. Stevens.

U.S. 3,647,411, Mar. 7, 1972, Appl. Apr. 2, 1970; 3 pp.

Carbon dioxide from the atmosphere is the only source of the C required by plants for synthesis of carbohydrates. In most cases plants are grown under conditions in which the CO_2 supply is a limiting factor in photosynthesis. Increasing the concentration of CO_2 much above that normally present in air (about 0.03 per cent) is generally toxic to plants after a short time. A method of supplying additional CO_2 to plants in nontoxic amounts consists of foliar application of a carbonated aqueous solution of micronutrients. For example, an aqueous solution containing H_3BO_3 6.73, $MnSO_4.H_2O$ 4.86, $CuSO_4$. 5 H_2O 0.25, $MoO_3.H_2O$ 0.75, $Co(NO_3)_2$. 6 H_2O 2.50, and Zn acetate dihydrate 1.68 g/1. was prepared. To this solution was added chelated Fe, followed by carbonation to a pressure of 100 psig with CO_2. The resulting solution was sprayed several times per week on tomato plants grown in soilless culture in a greenhouse with good results.

[*Fertilizer Abstracts*, **5** (6) (1972), 139.]

Liquid Fertilizers with Slow-Release Properties

A. F. Mitchell (to Galdonost Dynamics Ltd.).

U.S. 3,649,239, Mar. 14, 1972, Appl. New Zealand, July 24, 1968: 4 pp.

A slow-release liquid fertilizer is prepared by adding 0.5-1.0 per cent by wt of an alginate and adjusting the pH of the mixture to 6.5-7.5 to induce gelling. In an example, urea 21. H_3PO_4 (80 per cent) 12.6, KOH 8.6, alginate (seaweed extract) 0.57 and water 56.7 parts were mixed, giving a pH of 7.0. After application, the nutrient release rate can be increased by adding an alkali such as K_2CO_3 or Na_2CO_3 to the soil, or the rate can be decreased by applying a salt of a heavy metal such as Ca to catalyze gel formation.

[*Fertilizer Abstracts*, **5** (6) (1972), 140.]

Water-Gas Shift Conversion Process

A. M. Robin and J. P. Tassoney (to Texico, Inc.).

U.S. 3,652,454, Mar. 28, 1972, Appl. May 27, 1968; 6 pp.

Steam is reacted with the CO contained in water-gas in a converter comprised of a series of fixed beds of catalyst with interbed cooling. The catalyst, containing 85-95 per cent Fe_2O_3 and 5-15 per cent Cr_2O_3, is characterized by increasing activity with increasing pressure in the range 35-250 atm. The temperature of the gases leaving each bed is maintained at 30-100°F less than the corresponding equilibrium temperature. To offset catalyst deactivation the inlet and exit gas temperature of each bed are gradually increased as a log function of time on steam. These improvements result in a substantially constant composition of converted gas throughout the catalyst life. The overall CO conversion is 80-98 mole per cent for 2 yr on-stream. The converter can be operated at the same pressure as the water-gas generator.

[*Fertilizer Abstracts*, **5** (7) (1972), 161.]

Nitric Oxide Analysis Method

J. N. Harmann and R. M. Neti (to Beckman Instruments Inc.).

U.S. 3,652,227, Mar. 28, 1972, Appl. Dec. 15, 1969; 6 pp.

Nitric oxide in a gas stream is reacted with excess O_3 to completely convert the nitric oxide to NO_2. The excess O_3 is then scrubbed out of the gas stream, for example, with granular AgO which also removes SO_2, H_2S, halogen gases, and organic S compounds without affecting the NO_2. The gas is then analyzed for NO_2 content which is a function to the nitric oxide content of the original gas. The method is especially suited for monitoring air for pollution control.

[*Fertilizer Abstracts*, **5** (7) (1972), 161.]

Nitrophosphate Process

A. Y. Guery (to Badger N. V.).

U.S. 3,653,872, Apr. 4, 1972, Appl. Neth. Dec. 18, 1968; 4 pp.

Phosphate rock is acidulated with HNO_3 and NH_4HSO_4 wherein the NH_4 HSO_4 serves both as an acidulant as well as a precipitant for Ca as $CaSO_4$. The $CaSO_4$ is filtered off and converted to $(NH_4)_2SO_4$ and $CaCO_3$ by treatment with recycled gas containing NH_3 and CO_2. The $CaCO_3$ is filtered off and the filtrate is treated to crystallize $(NH_4)_2SO_4$. The crystals of $(NH_4)_2SO_4$ are heated at 160-200° which yields a melt comprised of NH_4HSO_4 and undecomposed $(NH_4)_2SO_4$. The melt is then heated at about 400° and contacted in a packed column or spray tower with a mixture of CO_2 and hot flue gases and (or) superheated steam whereby most of the residual $(NH_4)_2SO_4$ is decomposed, yielding a melt containing over 90 per cent NH_4HSO_4. The gases from decomposition are recycled to convert $CaSO_4$ to $(NH_4)_2SO_4$ and $CaCO_3$. The melt is recycled to the phosphate rock acidulation. The filtrate from the $CaSO_4$ filter is ammoniated to produce a solution containing ammonium phosphate and NH_4NO_3 which is used to prepare nitrophosphate fertilizers by usual methods. Use of NH_4HSO_4 in the acidulation replaces an equivalent amount of HNO_3 so that the $N:P_2O_5$ ratio in the product is about half that obtained in the conventional process.

[*Fertilizer Abstracts*, **5** (7) (1972) ,167.]

Ammonia Synthesis Catalyst

Kenzi Tamaru *et al* (to Tokyo Metrop Univ.).

U.S. 3,658,721, Apr. 25, 1972, Appl. Japan Feb. 6, 1969; 2 pp.

A new type of NH_3 synthesis catalyst consists of complex compounds prepared from an alkali metal or organo-alkali metal compound and a transition metal phthalocyanine or porphyrin. For example, 0.5 g of metallic Na was deposited on the inner wall of a glass U-tube. On the Na was deposited 0.1 g of Fe-phthalocyanine. The deposited substances were then heated at 200° in vacuo, forming a deep-colored complex catalyst of Fe-phthalocyanine-Na. The surface area of the catalyst was about Im^2/g. A synthesis gas mixture (140 ml) containing N_2 at a partial pressure of 10 cm Hg and H_2 at a partial pressure of 30 cm Hg was circulated over the catalyst for 20 hr. The reaction temperature was 260°. The yield of NH_3 was 4.60 ml (stp). Exposure of the catalyst to O_2CO had no appreciable effect on the catalytic activity.

[*Fertilizer Abstracts*, **5** (8) (1972), 000.]

Ammonia Synthesis Catalyst

Kenzi Tamaru *et al* (to Tokyo Metrop. Univ.).

U.S. 3,660,028, May 2, 1972, Appl. Japan Feb. 6, 1969; 3 pp.

A new type of NH_3 synthesis catalyst consists of a complex of an alkali metal, an alkali metal benzophenone ketyl, or an alkali metal salt of an aromatic hydrocarbon, with graphite. For example, a mixture of 2 g of graphite powder and 2 g of metallic Na was heated at 300° in vacuo in a glass U-tube. The resulting complex catalyst had a surface area of about 500 m^2/g. A synthesis gas mixture (114 ml) containing N_2 at a partial pressure of 5.8 cm Hg and H_2 at a partial pressure of 9.2 cm Hg was circulated over the catalyst for 12 hr. The reaction temperature was 300°. The yield of NH_3 was 2.1 ml (stp). The activity of the catalyst was not decreased appreciably in the presence of O_2 and CO.

[*Fertilizer Abstracts*, **5** (8) (1972), 000.]

Nitric Acid Manufacture

Gerard Aquinet, Jean Manoury, and Edouard Martin (to Ugine Kuhlmann S. A.).

U.S. 3,658,472, Apr. 25, 1972, Appl. France July 1, 1968; 8 pp.

Nitrous vapors from the catalytic combustion of NH_3 are bubbled through dilute HNO_3 with cooling. The exit vapors are passed through an oxidation zone and are again bubbled through HNO_3 of higher concentration with cooling. The operation is repeated in a plurality of stages, for example in a plate column. Vapors from an NH_3 burner are fed to the top plate. By means of a set of vertical chimneys and partitions between plates, acid from the top plate flows onto the plate immediately below it. The vapors from the top plate are also fed to the plate immediately below. Each plate is provided with a cooling coil. A vapor space above each plate is provided an oxidation zone for the vapors fed to the plate below. The column is operated at 60-120 psi, and the temperature of the first plate is 95-115°. Thus, cooling,drying, oxidation, and absorption are carried out jointly in a single apparatus.

[*Fertilizer Abstracts*, **5** (8) (1972), 000.]

Utilizaton of Byproducts of Phosphate Manufacture

Heniz Harnisch *et al* (to Knapsack A. G.).
U.S. 3,656,898, Apr. 18, 1972, Appl. Ger. Feb. 17, 1965; 3 pp.

Low-valent P compounds in waste byproducts obtained in the production of organic and inorganic P compounds are introduced into a P-O_2 flame operated with excess O_2. For example, about 10.2 per cent of an aqueous 55 per cent Na_2HPO_3 solution was introduced into a P-O_2 flame and the resulting P_4O_{10} was absorbed in a solution of phosphoric acid to produce superphosphoric acid according to the method of U.S. 3,526,482 (FA 4,25). Other examples described the utilization of byproducts from PH_3 manufacture and a distillation residue from organic phosphate production.

[*Fertilizer Abstracts*, **5** (8) (1972), 000.]

Gyspum Granules for Agricultural Use

J. F. Wilson (to Phillips Petroleum Co.).
U.S. 3,660,068, May 2, 1972, Appl. Dec. 9 1969; 3 pp.

Unwashed byproduct gypsum from the manufacture of wetprocess H_3PO_4 is granulated using a solution of $(NH_4)_2HPO_4$ to provide a bonding agent. Washed byproduct gypsum or natural gypsum (100-mesh size) is granulated using solutions of NH_4NO_3, urea, KCl, or $(NH_4)_2HPO_4$ or their mixtures.

[*Fertilizer Abstracts*, **5** (8) (1972).]

Controlled-Release Liquid Fertilizers

Galdonost Dynamics (N. Z.)Ltd.

Brit. 1,271,575 Apr. 19, 1972, Appl. July 24, 1968; 5 pp.

Potassium alginate solution is prepared by treating seaweed with aqueous KOH. To the resulting solution is added H_3PO_4 until the pH is 4.2-8 (preferably 6-5.7-5). The H_3PO_4 suppresses the ionization of the alginate anion and the solubility of the K, forming a gel. The solubility of added compounds such as urea is also suppressed by acidulation and gel formation. At pH below 4.2 there is little or no release of chemicals from the gel. As the pH is increased the solubility increases, and above pH 8 the alginate has little or no effect on solubility. When such a fertilizer having a pH above 7 is applied to acid soils the initial release of nutrients is relatively rapid, As the soil acids react with the alginate the erlease rate becomes slower. It is thereby possible to design fertilizer especially suited for specific soils and crops. The release rate can be changed after application. Examples give formulations for NPK grades 10-3-5, 10-5-5, 10-4-6, 8-6-8, and 7-4-11.

[*Fertilizer Abstracts*, **5** (8) (1972), 000.]

Pyrite-Pyrrhotite from Rajasthan

National Metallurgical Laboratory (CSIR), have studied the beneficiation of pyrites-pyrrhotite samples from Saladipura (Rajasthan) containing 23 per cent sulphur to produce a concentrate assaying 39 per cent sulphur to be used in the fertilizer industry.

The sample was crushed to 10 mesh and 500 g. of the crushed sample was ground in a rod mill and was conditioned with the reagents (potassium ethyl xanthate and pine oil) at 50 per cent solids and then diluted to 30 per cent solids for flotation tests. The optimum conditions were found to be 93 per cent—200 mesh with 0.24 kg/te of KEX, 0.045 kg/te of pine oil and 3 per cent of sulphuric acid (pH 5.2-5.7). Under these conditions, concentrate obtained was 53.3 per cent by weight assaying 40.5 per cent sulphur with 91.8 per cent sulphur recovery.

After determining the optimum conditions, continuous pilot plant studies were carried out using the following alternate flow sheets, viz. (i) straight flotation and (ii) tabling followed by flotation.

The results showed that 0.24 kg/te KEX 0.03 kg/te pine oil and 3.0 kg/te of sulphuric acid along with reclaimed water were the optimum reagents required under which a concentrate weighing 48.5 per cent and assaying 41.5 per cent sulphur with a recovery of 94.9 per cent was produced.

By the second method the grade of the concentrate was high (46.8 per cent) but the recovery was only 63.8 per cent.

[*NML Tech. J.*, **14** (2) (1972), 56]

Fertilizer Plant in Andhra Pradesh

The first fertilizer plant under the joint sector policy of the Government is being set up in the coastal town Kakinada. The project, costing Rs. 125 crores, is sponsored by the Barium Chemicals Ltd. of Kothagudem in collaboration with Snam Progetti and ENI of Italy. The Government of India is also participating. The fertilizer complex which is being established after detailed feasibility studies would have a capacity of 900 tes of ammonia, 1000 tonnes of urea and 900 tes of diammonium phosphate a day. The plant will use fuel oil and coal as feedstocks.

Conference on Thermal Analysis

The Fourth International Conference on Thermal Analysis, organized by the International Confederation for Thermal Analysis in cooperation with the Analytical Section of the Hungarian Chemical Society will be held at Budapest during July 8 to 13, 1974, under the presidentship of Prof. E. Pungor. The conference will divided into the following sections: (1) Theory and Methodics, (2) Inorganic Chemistry (3) Organic and macromolecular chemistry (4) Earth Sciences (5) Applied sciences and (6) Instrumentation. Abstracts of papers should be submitted before January 31, 1974. The manuscripts of papers should be submitted during the conference. The proceedings of the conference will be published.

Coal Mines Authority Ltd.

Government of India has constituted a new company, Coal Mines Authority Ltd., which will manage 571 non-coking mines nationalized by the Government in the States of Bengal, Bihar, Assam, Meghalaya, Maharashtra, M.P., Orissa and Nagaland. A total of Rs. 830 crores is proposed in the Fifth Plan to nearly double the present coal production; by the end of the fifth plan the production has been fixed at 143 million tonnes. With this vast nation-wide network, CMA has come to stand as one of the biggest employers employing 3,52,000 workers. Its total production is 44,55,000 tonnes per month.

Dr. K. R. Chakravorty, Managing Director FCI Ltd., has been given 'Scientia et Divulgatio 1973' award by the International Catalyst Conference held at Vienna in April 1973. The award, a gold medal, has been won by him in recognition of his theory of the concept of unit of universal wave and unified wave continuum. The theory embodies a fundamental law of nature explaining manifestations of natural phenomena in terms of phases exhibiting their intensive properties through a process of evolution in sequence.

Award

Sri R. C. P. Sinha, Technologist in Physical Research Wing of Planning and Development Division, FCI Ltd. Sindri has been recently awarded Ph.D. Degree in Science by Bhagalpur University. The title of his thesis is Spectroscopic Studies of Trace Elements and Low Content Impurities in some Materials.

The estimation of trace and low content elements in materials e.g. soils, fertilizer raw materials, base materials and fertilizer products has been a challanging problem in fertilizer technology. The materials selected by Dr. Sinha for the studies are important from agricultural and industrial points of view. He has developed methods for the study of many of the selected materials and adopted them with necessary modifications for the others. For the present work, he has used spectrographic and atomic absorption spectrophotometric techniques.

STATISTICS

TABLE 1—NITROGEN CAPACITY IN INDIA BASED ON DIFFERENT FEEDSTOCKS

Particulars	1965-66		1960-61		1955-66		As on 1.11.72		1973-74		Firmed projects 1975-76		Likely by 1978-79	
	Qty., '000 tonnes	Percentage	Qty., '000 tonnes	Percentage	Qty., '000 tonnes	Percentage	Qty., '000 tonnes	Percentage	Qty., '000 tonnes	Percentage	Qty., '000 tonnes	Percentage	Qty., '000 tonnes	Percentage
(1) Naphtha					112	19.1	1,039	70.9	1,707	74.8	2,179	52.4	2,436	34.8
(2) Fuel oil/heavy stock											631	15.1	3,208	45.8
(3) Natural/associated gas							91	6.2	243	10.6	458	11.0	458	6.6
(4) Coal	10*	10.4	10*	4.0							684	16.4	84	9.8
(5) Coke	70	73.0	80	32.3	80	13.7	80	5.5	80	3.5	10	0.2	10	0.1
(6) Lignite					70	12.0	70	4.8	70	3.1	70	1.7	70	1.0
(7) Coke Oven gas			47	18.9	212	36.2	80	5.5	80	3.5	70	1.7	70	1.0
(8) By-product from coke oven gas	15	15.6	20	8.1	20	3.4	20	1.4	20	0.8	20	0.4	20	0.3
(9) Electrolytic hydrogen	1	1.0	91	36.7	91	15.6	84	5.7	84	3.7	4	0.1	4	—
(10) Imported ammonia											40	1.0	40	0.6
	96	100.0	248	100.0	585	100.0	1,464	100.0	2,284	100.0	4,166	100.0	7,000	100.0

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*Wood gasification.

[S. Venkataraman and P. Jayantha Rao, *Plenning for Self-Sufficiency—Raw Materials for Nitrogenous Fertilizer Industry*, paper read at the FAI Seminar on Fertilizers in India in the Seventies held at New Delhi on December 18-19, 1972]

TABLE 2—COUNTRYWISE IMPORTS OF PHOSPHATE ROCK IN INDIA

(tonnes)

S. No.	Country	1967-68	1968-69	1969-70	1970-71	1971-72
1.	Africa, West	4,800	—	—	—	—
2.	Algeria	34,625	—	—	—	—
3.	Hungary	—	—	—	—	—
4.	Japan	—	4,200	—	—	—
5.	Jordan	3,67,547	432,286	296,993	47,110	348,904
6.	Kenya	—	7,700	—	—	—
7.	Morocco	134	20,404	14,387	182,739	86,474
8.	Senegal	—	9,957	—	27,432	—
9.	Togoland	18,075	—	—	—	—
10.	Tunisia	19,569	47,096	—	18,230	85,896
11.	U.A.R.	59,715	73,902	47,292	29,797	—
12.	U.S.A.	94.857	249,659	287,716	450,638	320,347
13.	Yugoslavia	4,714	—	—	—	—
	Total:	604,036	845,204	646,338	755,946	841,621

[S. Ramchandran, *Planning for Self Sufficiency—Phosphate Rock and Sulphur Situation in India*, paper read at the FAI Seminar on Fertilizers in India in the Seventies held at New Delhi on December 18-19, 1972]

TABLE 3—MANUFACTURERS AND LICENSED CAPACITY OF SUPERPHOSPHATE
(as on 30th September 1972)

	Name of Factory	Capacity, te	
		Material	P_2O_5
South		526,610	84,330
	Andhra Pradesh	166,230	26,590
1.	Andhra Fertilizers Ltd., Tadepalle	40,000	6,400
2.	Andhra Sugars Ltd., Tanuku	33,530	5,360
3.	Hyderabad Chemicals & Fertilizers Ltd., Maula Ali	41,900	6,700
4.	Krishna Industrial Corporation, Nidadavole	50,800	8,130
	Kerala	44,700	7,150
5.	Fertilizers & Chemicals, Travancore Ltd., Alwaye	44,700	7,150
	Mysore	74,170	11,860
6.	Chamundi Chemicals & Fertilizers Ltd., Munirabad	40,640	6,500
7.	Mysore Chemicals & Fertilizers Ltd., Belagula	33,530	5,360
	Tamil Nadu	241,510	38,730
8.	Kothari (Madras) Ltd., Ennore	44,700	7,150
9.	Coimbatore Pioneer Fertilizers Ltd., Coimbatore	40,640	6,500
10.	E.I.D.-Parry Ltd., Ranipet	40,000	6,400
11.	Premier Fertilizers Ltd., Cuddalore	40,640	6,500
12.	Shaw Wallace & Co., Avadi	75,530	12,180
West		228,660	36,580
	Gujarat	90,530	14,480
13.	Adarsh Chemicals & Fertilizers Ltd., Udhna	33,530	5,360
14.	Alembic Chemical Works Co. Ltd., Baroda	23,470	3,760
15.	Anil Starch Products Ltd., Bhavnagar	33,530	5,360
	Maharashtra	138,130	22,100
16.	Bharat Fertilizer Industries Ltd., Bombay	22,500	3,600
17.	Dharamsi Morarji Chemical Co. Ltd., Ambernath	73,160	11,710
18.	Eastern Chemical Co. Ltd., Bombay	5,590	890
19.	Western Chemical Industries Ltd., Bombay	3,350	540
20.	West India Chemicals Ltd., Loni-Kalbhore	33,530	5,360

TABLE 3 (*Continued*)—MANUFACTURERS AND LICENSED CAPACITY OF SUPERPHOSPHATE
(as on 30th September 1972)

Name of Factory	Capacity, te	
	Material	P_2O_5
Central	342,960	54,870
Madhya Pradesh	75,000	12,000
21. Dharamsi Morarji Chemical Co. Ltd., Kumahari	75,000	12,000
Rajasthan	75,000	12,000
22. Hindustan Zinc Ltd., Debari	75,000	12,000
Uttar Pradesh	60,960	9,750
23. Ralli Chemicals Ltd., Magarwara	60,960	9,750
Delhi	132,000	21,120
24. D.C.M. Chemical Works, Delhi	132,000	21,120
East	151,530	24,240
Assam	33,530	5,360
25. Associated Industries (Assam) Ltd., Chandrapur	33,530	5,360
Bihar	23,470	3,760
26. Bihar State Superphosphate Factory, Sindri	23,470	3,760
West Bengal	94,530	15,120
27. Jayshree Chemicals & Fertilizers Ltd., Khardah	33,530	5,360
28. Phosphate Co. Ltd., Rishra	61,000	9.760
Total:	1,249,760	199,930

Source: FAI Statistics 1971-72
[V. R. Rajagopalan, *Superphosphate and Mixture Industry in the Seventies*, paper read at the FAI Seminar on Fertilizers in India in the Seventies, held at New Delhi on Dec. 18-19, 1972]

TABLE 4—MANUFACTURERS AND LICENSED CAPACITY OF COMPLEX FERTILIZERS
(as on 30th September 1972)

Name of Factory	Capacity, te		
	Material	N	P_2O_5
I. IN PRODUCTION			
(a) Ammonium phosphate sulphate			
South	—	42,540	44,600
1. Fertilizers and Chemicals, Travancore Ltd., Alwaye (Kerala)			
20-20-0	171,500	34,300	34,300
2. E.I.D. Parry Ltd., Ennore (Tamil Nadu)			
16-20-0	51,480	8,240	10,300
Total:	—	42,540	44,600
(b) Diammonium phosphate			
West	108,000	21,600	51.840
1. Gujarat State Fertilizers Co. Ltd., Baroda (Gujarat)			
18-46-0@ 18-27-3	108,000	21,600	51,840
Total:	108,000	21,600	51,840

TABLE 4 (*Continued*)—MANUFACTURERS AND LICENSED CAPACITY OF COMPLEX FERTILIZERS (as on 30th September 1972)

Name of Factory			Capacity, te			
			Material	N	P_2O_5	
(c) Nitrophosphate West			180,000	36,000	36,000	
1. Fertilizer Corporation of India Ltd., Trombay (Maharashtra)	20-20-0@ 20-20-2 15-15-15 18-18-9 15-7.5-15 15-7.5-10 14-10.5-14 etc.		180,000	36,000	36,000	
Total:			180,000	36,000	36,000	
(d) Urea ammonium phosphate South			260,000	73,000	73,000	
1. Coromandel Fertilizers Ltd., Visakhapatnam (A.P.)	28-28-0@ 20-20-0 22-22-11 14-35-14		260,000	73,000	37,000	
Total:			260,000	73,000	73,000	
(e) NPK complex fertilizers South			360,000	67,400	85,000	
1. Madras Fertilizers Ltd., Manali (Tamil Nadu)	17-17-17 14-28-14 28-28-0 18-36-0 24-12-12 11-22-22	90,600 72,500 54,500 54,400 54,400 36,300	360,000[a]	67,400	85,000	
Total:			360,000	67,400	85,000	
Grand Total for I:			—	240,540	290,440	
II. UNDER IMPLEMENTATION						
(a) Diammonium phosphate South			28,000	5,040	12,880	
1. Southern Petrochemical Industries Corpn., Ltd., Tuticorin (Tamil Nadu)	18-46-0		28,000	5,040	12,880	Mid 1974
West 2. Zuari Agro Chemical Co. Ltd., San Coale (Goa)	18-46-0		—	—	—	Jan 1973
Total:			28,000	5,040	12,880	—
(b) Urea ammonium phosphate West			150,000	42,000	42,000	
1. Zuari Agro Chemical Co. Ltd., San Coale (Goa)	28-28-0		150,000	42,000	42,000	Jan 1973
Total:			150,000	42,000	42,000	

TABLE 4 (*Continued*)—MANUFACTURERS AND LICENSED CAPACITY OF COMPLEX FERTILIZERS
(as on 30th September 1972)

Name of Factory		Capacity, te			
		Material	N	P_2O_5	
(c) Nitrophosphate West		550,000	110,000	110,000	
1. Fertilizer Corporation of India Ltd., Trombay (Maharashtra)*	20-20-0	550,000	110,000	110,000	1977
East		375,000	75,000	75,000	
2. Fertilizer Corporation of India Ltd., Haldia (West Bengal)	20-20-0	375,000	75,000	75,000	1977
	Total:	925,000	185,000	185,000	
(d) NPK complex fertilizers South		—	62,480	168,000	
1. Cochin Fertilizer Project, Ambelamedu (Kerala) (Phase II)	17-17-17 14-28-14 28-28-0 18-36-0 11-22-11	485,000	40,000	115,000	1976
2. Southern Petrochemical Industries Corporation Ltd., Tuticorin (Tamil Nadu)	10-26-26 15-15-15	128,000 32,000	22,480	53,000	Mid 1974
West		—	34,680	127,000	—
3. Zuari Agro Chemical Co. Ltd., San Coale (Goa)	18-18-18[b]				Jan 1973
4. Indian Farmers Fertilizer Coop. Ltd. Kandla (Gujarat)	10-26-26 12-32-16 14-36-12	92,800 92,800 189,900	34,680	127,000	end 1974
	Total:	—	97,160	295,000	
	Grand Total for II:	—	329,200	534,880	
III. APPROVED IN PRINCIPLE					
(a) Diammonium phosphate West		250,000	45,000	115,000	
1. Konkan Fertilizers Ltd.,[c] Sheva Nohva (Maharashtra)	18-46-0	250,000	45,000	115,000	1975
	Total:	250,000	42,000	115,000	

TABLE 4 (*Continued*)—MANUFACTURERS AND LICENSED CAPACITY OF COMPLEX FERTILIZERS
(as on 30th September 1972)

Name of Factory		Capacity, te			
		Material	N	P_2O_5	
(b) Urea ammonium phosphate South		28,500	8,000	8,000	
1. Coromandal Fertilizers Ltd.* Visakhapatnam (A.P.)	28-28-0	28,500	8,000	8,000	1977
	Total:	28,500	8,000	8,000	
	Grand Total for III :	—	53,300	123,000	—
	Grand Total for I, II, & III:	—	622,740	948,320	—

@ = Capacity is related to this grade

* = Capacity under expansion.

a = Total capacity of the unit for fertilizer purposes is 164,000 tonnes N and 85,000 tonnes of P_2O_5 per annum comprising 210,000 tonnes of urea and 360,000 tonnes of NPK complex fertilizers of various grades. Of the latter, at present, two grades 17-17-17 and 14-28-14 are manufactured contributing a total capacity of 85,000 tonnes of P_2O_5 and 67,400 tonnes of N. Their exact gradewise share is not available.

b The project when commissioned in January 1973, besides urea it would manufacture urea ammonium phosphate, diammonium phosphate, and NPK complex fertilizer (18-18-18) to a total capacity of 150,000 tonnes of material (equivalent to 42,000 tonnes of P_2O_5). Their materialwise break-up is not yet finalised.

c The project has since been dropped.

Sources: FAI Statistics 1971-72

[V. R. Rajagopalan, *Superphosphate and Mixtures Industries in the Seventies*, paper read at the FAI Seminar on Fertilizers in India in the Seventies held at New Delhi on Dec. 18-19, 1972]

TABLE 5—ESTIMATED TIME-LAG BETWEEN INVENTION AND INNOVATION

S. N.	Invention	Interval, Years
1.	Cotton picker	53
2.	Spinning jenny	5
3.	Spinning machine (water frame)	6
4.	Spinning mule	4
5.	Power steering	6
6.	Steam engine (Watt)	11
7.	Steam engine (Newcomen)	6
8.	Jet engine	14
9.	Turbojet	10
10.	Fluorescent lamp	79
11.	Wireless telephone	8
12.	Wireless telegraph	8
13.	Triode vacuum tube	7
14.	Radio (Oscillator)	8
15.	Gyrocompass	56
16.	Self-winding watch	6
17.	Xerography	13
18.	Ball point pen	6
19.	Zipper	27
20.	Safety razor	9
21.	Long playing record	3
22.	Magnetic recording	5
23.	Shell moulding	3
24.	Titanium reduction	7
25.	Electrical precipitation Petroleum Production	25
26.	Distillation of hydrocarbons with heat and pressure	24
27.	Distillation of gas oil with heat and pressure	3
28.	Continuous cracking (Holmes & Manley)	11
29.	Continuous cracking (dubbs)	13
30.	Clean circulation	3
31.	Tube and tank process	13
32.	Cross process	5
33.	Houdry catalytic cracking	9
34.	Fluid catalytic pellet	13
35.	Gas lift for catalyst cracking	13
36.	Moving bed catalytic cracking	8
37.	DDT	3
38.	Streptomycin	5
39.	Freon refrigerant	1
40.	Hardening of fat	8
40.	Plexiglass, lucite	3
42.	Nylon	11
43.	Terylene	12
44.	Crease resistant fabric	14

[A. Neelameghan and S. Seetharama, *Seminar Reporteur*, 3 (1) (1973), 24]

TABLE 6—AVERAGE RATE OF DEVELOPMENT OF SELECTED TECHNOLOGICAL INNOVATIONS

Particulars	Average Time Intervals, years		
	Incubation period	Commercial Development	Total
1. Time Period			
1.1 Early twentieth century (1885-1919)	30	7	37
1.2 Post World War-I (1920-44)	16	8	24
1.3 Post-World War-II (1945-64)	9	5	14
2. Type of Market application			
2.1 Consumer	13	7	20
2.2 Industrial	28	6	34
3. Source of Development			
3.1 Private industry	24	7	31
3.2 Federal government	12	7	19

[A. Neelameghan and S. Seetharaman, *Seminar Reporteur*, **3** (1) (1973), 26]

TABLE 7—DISCOVERY-TO-DEVICE TIME-LAG

S. N.	Invention	Year of		Time-lag between c and d
		Discovery of principle	Development of device or use	
a	b	c	d	e
1	Internal combustion engine	1710	1892	182
2	Photography	1727	1839	112
3	Aerial flight	1809	1903	94
4	Telephone	1823	1876	53
5	Radar	1889	1935	48
6	Gamma ray	1896	1939	43
7	Atomic power release	1932	1945	13
8	Transistor	1940	1948	8
9	Laser	1958	1960	2

[A. Neelameghan and S. Seetharaman, *Seminar Reporteur*, **3** (1) (1973), 25]

TABLE 8—TIME-LAG DIFFERENTIAL BETWEEN SELECTED COUNTRIES

[Intercountry diffusion of technology has been indicated; data regarding the time lag of each of a few countries behind the pioneering country are presented here]

Sl. No.	Process/Technique	Year of Introduction	Pioneer country	No. of years of Lag after Pioneer Country					
				Austria	France	Germany	Italy	Sweden	UK
1	Oxygen	1952	Austria	0	4	5	12	4	8
2	Casting†	1952	Austria	0	8	2	6	11	8
3	Press	1963	Sweden	3	2	2	2	0	1
4	NC‡‡	1955	UK	8	2	7	5	3	0
5	Loom	1953-4	France	7	0	1	6	3	4
6	Kiln**	1943	Sweden	9	1	11	3	0	0*
7	Steel marking	1950	Sweden	—	10	3	12	—	0
8	Glass	1958	UK	—	8	8	7	—	0
9	Transfer line	1947	France-UK	—	0	7	3	8	0
10	Malting	1959	Sweden-UK	—	7	—	—	0	0
		Mean		4.5	4.2	5.1	6.2	3.2	2.3

* The extreme value (1902) for UK omitted. † Continuous casting of steel
‡ Numerical control of metal working machine tools
** Tunnel kiln for brick-making

[A. Neelameghan and S. Seetharaman, *Seminar Reporteur*, **3** (1) (1973), 23]

TABLE 9—MAJOR NEW IDEAS DURING DIFFERENT PERIODS

Main Subject	Number of Major New Ideas and Subjects Created During		
	1451-1700 (250 y)	1701-1900 (200 y)	1901-50 (50 y)
Mathematics	9	24	21
Physics	3	21	68
Engineering	1	23	46
Chemistry	0	36	80
Technology	0	21	70
Biology	2	4	8
Geology	1	16	8
Botany	1	7	4
Agriculture	0	2	2
Zoology	0	4	4
Medicine	4	21	80
Total:	21	180	391

[A. Neelameghan, *Seminar Reporteur*, **3** (1) (1973), 7]

TABLE 10—WORLD OUTPUT OF SCIENTIFIC AND TECHNICAL ARTICLES IN PERIODICALS

Sl. No.	Subject	No. of Articles	
		1960	1970 (est.)
1	Mathematics	15,000	30,000
2	Physics	75,000	150,000
3	Engineering	155,000	275,000
	Civil	15,000	15,000
	Mechanical	10,000	20,000
	Electrical and Electronic	80,000	150,000
	Aero space	35,000	75,000
	Industrial	15,000	15,000
4	Chemistry	150,000	290,000
5	Metallurgy	35,000	50,000
6	Biology	150,000	260,000
7	Geosciences	91,000	158,000
8	Agriculture	150,000	260,000
9	Medicine	220,000	390,000
10	Psychology	15,000	30,000
11	Other Subjects	929,000	1,882,000
	Total:	1,985,000	3,780,000

[A. Neelameghan, *Seminar Reporteur*, **3** (1) (1973), 8]

TABLE 11—TECHNOLOGICAL BALANCE OF PAYMENT (1964)

Country	% of World Total		
	Receipt	Payment	Balance
USA	57	12	+45
UK	12	11	+ 1
Germany (FR)	6	14	− 8
France	5	11	− 6
Other countries of W. Europe	18	25	− 7
Japan	1	13	−12
Other developed countries	1	6	− 5
Developing countries	1	8	− 7

The international exchange of know-how has been shown by a technological balance of payment. Therein a country's payments to other countries for technical know-how, licence and patents received with its receipts for 'selling' such items can be compared.

[A. Neelameghan & S. Seetharaman, *Seminar Reporteur*, **3** (1) (1973), 27]

TABLE 12—R & D EXPENDITURE IN THE PRIVATE SECTOR EXPRESSED AS PERCENTAGE OF TOTAL EXPENDITURE/ PRODUCTION IN INDIA, 1970-71

% to total expenditure/ production	Total Number of Companies	
	R & D expenditure as percentage of total expenditure	R & D expenditure as percentage of value of total production
Upto 0.50	14	17
0.51 - 1.00	9	14
1.01 - 1.50	10	7
1.51 - 2.00	5	3
2.01 - 3.00	7	6
3.01 - 4.00	3	3
4.01 - 5.00	2	1
5.01 - 7.50	1	—
7.51 - 10.00	—	1
10.01 and above	1	—
Total:	52	52
Average	1.11%	0.95%

[D. N. Trivedi, *Indian Chem. J.*, **7** (5) (1972), 17]

TABLE 13—ESTIMATED R & D EXPENDITURE IN CENTRAL, STATE AND PRIVATE SECTORS IN INDIA

(Rs. in crores)

	1958-59		1965-66		1970-71		1971-72	
	Expenditure	% to total	Expenditure	% to total	Expenditure	% to total	Expenditure (Revised estimate)	% to total (Budget estimates)
(a) Central Sector (including universities)	27.66	96.0	79.12	93.0	146.20	84.3	182.74	85.4
(b) State Sector	1.00	3.5	3.51	4.1	12.58	7.3	13.84	6.5
(c) Private Sector	0.15	0.5	2.43	2.9	14.59	8.4	17.46	8.1
Total:	28.81	100.0	85.06	100.0	173.37	100.0	214.04	100.0

[D. N. Trivedi, *Indian Chem. J.*, **7** (5) (1972), 17]

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QUARTERLY BULLETIN OF THE PLANNING & DEVELOPMENT DIVISION
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Vol. 10 JULY–DECEMBER, 1973 Nos. 3 & 4

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UDC 631.81.095.337: 535.214.4: 631.42

The mobility and retention characteristics of five micronutrients, viz. iron, manganese, molybdenum, zinc and cobalt, have been studied and discussed through three different types of soil, viz. Sindri red sandy clay loam, Ranchi clay loam and Amraoti (Maharastra) black loam, using gamma-emitting radio tracers ^{59}Fe, ^{54}Mn, ^{99}Mo, ^{65}Zn, and ^{60}Co. Time dependence of micronutrient mobility and the variation of retention with pH of the soil and nutrient concentration have also been investigated.

Radiotracer Studies on the Mobility and Retention of Micronutrients in Soil

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Introduction

Amongst the mineral contents of soils some elements are only beneficial while some others are essential for plant growth. Sodium, aluminium, vanadium and silicon, etc. fall in the first category. The essential elements are directly involved in plant nutrition apart from correcting some unfavourable microbiological or chemical conditions of the external medium. Moreover, their deficiency would make a plant unable to complete its vegetative or reproductive stage of the life cycle. Such deficiency is normally specific and can be prevented or corrected by supplement of the element in question. The essential elements are classified in two groups on the basis of nutritional requirements, viz. (i) **Macronutrients**—Nitrogen, phosphorus, potassium, calcium, magnesium and sulphur, which are cellular constituents indispensable for life, and (ii) **Micronutrients**—iron, manganese, zinc, boron, carbon, molybdenum, cobalt and chlorine, which are generally responsible for correcting the nutritional deficiency of plants and crops, have minor beneficial effects in improving certain crop yields[1] and behave as catalytic agents[2] in cellular metabolism, particularly in photosynthesis and nitrogen fixation.

The role of micronutrients in plant nutrition and their distribution in Indians soils have already been reported[3]. Micronutrients are supplied to plants and crops through the soil or foliar application by spraying. But spraying has two major disadvantages, viz. (i) the treatment is temporary and (ii) nutrient supply is very often incompatible. Therefore, plants and crops normally uptake the micronutrients from the soil, either directly from the soil solution or by exchange of ions between plant roots and soil colloids[4]. The shortfall of nutritional elements in soil is overcome by regular feeding as required, but their mobility or flow in soils is not a simple process; it involves different types of soil interactions. The portion of applied nutrients available for plants and crops actually depends on several factors, like adsorption or immobilization, diffusion, mobility, retention, etc. These characteristics of micronutrients through soil are, therefore, of considerable importance in plant nutritional studies and form vital problems in soil physics. The present investigation deals with mobility and retention characteristics of five micronutrients, viz. iron, manganese, molybdenum, zinc and cobalt, through three different types of soils, viz. Sindri red sandy clay loam, Ranchi clay loam and Amraoti black loam.

Since there is almost complete analogy between the mobility of radio-tagged and untagged species through the soil, gamma-emitting radiotracers ^{59}Fe, ^{54}Mn, ^{99}Mo, ^{65}Zn and ^{60}Co have been used for the investigation, However, there are some limitations to this analogy[5]. The process of adsorption, flow of tagged nutrients with sinks, particularly time dependent sinks, isotopic mass defect, self-diffusion, etc., form the major limitations. The isotopes used in these investigations being of long half-lives compared to the duration of the experiment, the limitation due to time dependent sink has been eliminated. In case of ^{99}Mo, half-life being comparatively less (67 hr), necessary decay corrections have been made. The error due to isotopic mass defect is prominent only when the kinetic coefficients of the carrier and the radio tracer are different. This is virtually negligible here because the chemical form of both are taken to be the same. The process of adsorption and self-diffusion are of course involved in the present investigation partly influencing the mobility and retention of the micronutrients in soil.

Experimental

Representative soil samples having pH values between 6.5 and 8.5 were collected from Sindri, Ranchi and Amraoti from 0 to 25 cm. depth. The pH values of Sindri soil were also changed to 3.9 and 7.4 from 6.5 by standard methods[6]. Their other important characteristics are given in Table 1. They were air-dried, crushed, passed through 100 sieve (BSS) and granules of size -1.5 mm. were selected for the investigations.

Each experimental tube of inner diam. 4 cm, length 32 cm. and made of pyrex glass was provided with seven side openings of 1 cm. diam. at 3 cm. regular intervals and ended in a tapered portion of 4 cm. length. End of the tube was covered with perforated perspex disc followed by glass wool. The side openings were utilized for sample collection at different heights for chemical analysis and normally kept closed by rubber bungs. Every tube was filled with 200 g. of processed soil with approximate compactness of 1.1 g. dry soil/ml.; thereafter, the column was soaked with redistilled water with 40 per cent of its predetermined[7] Mwhc (maximum water holding capacity) and used for the experiment.

Each radiotracer was diluted to a strength of 10μci/ml. and 5 ml. of it was mixed with 15 ml. of inactive carrier. Ionic concentration of micronutrient in every tagged solution was kept 2 mg./ml. by adjustment of the strength of inactive carrier and radiotracer specific activity. 20 ml. of tagged solution was then added to the top of the previously wet soil column. After the solution had soaked into the soil, two more rinsings were added and the nutrient mobility was studied. For nutrient retention studies, the soil column was then left overnight, leached with 500 ml. of redistilled water and then assessed for γ-activities at various depths. Tracer concentrations were also increased to two and four times for further investigations. ^{59}Fe, ^{54}Mn, ^{60}Co and ^{65}Zn were all taken in chloride form* in hydrochloric acid (dil.) whereas ^{99}Mo was used as ammonium molybdate in ammonia solution.

The experimental tube was mounted on a vertically moving platform along a metre scale. The entire system was shielded by 2.5 cm. thick lead brick-lining through which the collimated γ-rays from the soil in the experimental tube were projected on the γ-detector, which was 1″×1″ NaI (Tl) crystal mounted on RCA 6199 Photomultiplier tube and coupled with a single channel γ-spectrometer. The detector was set at best feasible geometry for assessing the sample at a particular horizontal level at a time (Fig. 1). The spectrometer was calibrated with standard γ-emitters of suitable energy ranges and activities. ^{59}Fe, ^{54}Mn, ^{99}Mo, ^{60}Co and ^{65}Zn were assessed in terms of count rates at their respective photopeaks. Counting at each position was continued for a sufficiently long time to minimize the effect of statistical fluctuations. Half-lives of ^{59}Fe, ^{54}Mn, ^{60}Co and ^{65}Zn being long compared to the time of the experiment, no decay corrections were required while using them.

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*The usual form available at the Bhabha Atomic Research Centre, Bombay.

TABLE 1—CHARACTERISTICS OF SOIL SAMPLES

Sample No.	Location	Texture	Type	Mwhc, cc/100 g.	pH	Compactness, g. dry soil/ml.	Sand, %	Silt, %	Clay, %	C.E.C., m.eq./100 g.
1.	Sindri (Bihar)	Red Sandy Clay Loam (0–25 cm.)	Mainly Illite	50	6.5	1.12	58	5	29	12.6
2.	Ranchi (Bihar)	Clay Loam (0–25 cm.)	Mainly Keolinite	50	4.9	1.15	42	20	38	20.3
3.	Amraoti (Maharashtra)	Black Loam (0–25 cm.)	Mainly Montmorillonite	50	8.5	1.10	31	22	27	52.9

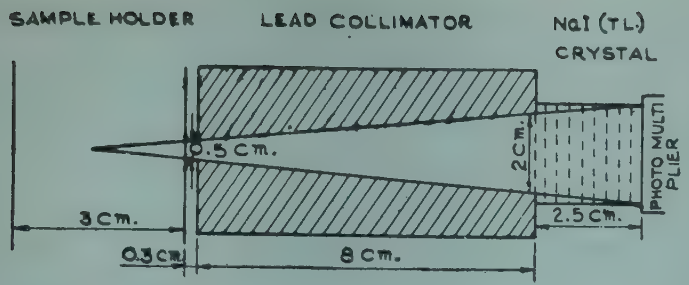

Fig. 1—Sample to Detector Geometry.

But ^{99}Mo being short-lived (67 hr), results were corrected fot its decay.

For assessing γ-activity of the leachets, a well scintillation detector with 2″×1.75″ NaI (Tl) crystal coupled with a single channel pulse height analyzer was used. The crystal-well measured 1.5″ deep and 0.7″ wide.

Replicate determinations were made with every soil and nutrient, but data for a single have been presented in each case. The radioactivity and the percentage of nutrient retained at various depths of the soil column were assessed by counting at that particular level.

Results and Discussion

Immediately after the addition of radio-tagged micronutrient to the soil columns, their percentage distributions at various depths was recorded by γ-spectrometry. The rate of nutrient mobility was found to fluctuate at the beginning, but the variation ceases in 24 hours with the distribution pattern remaining unchanged thereafter. Fig. 2 shows the percentage distribution of zinc at various depths of soil column. Daily record has been presented in the figure for a period of 15 days. The results confirm that at initial time gap of 24 hr, after the addition of the nutrient solution, was sufficient for retention and other studies discussed here.

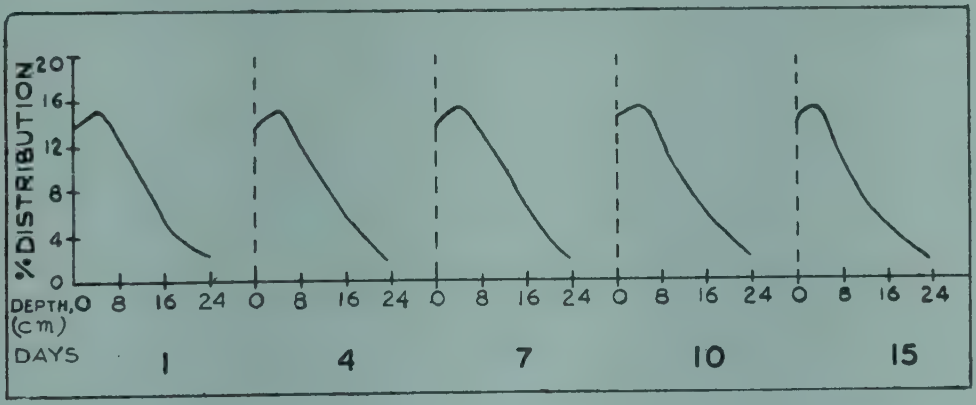

Fig. 2—Daily Record of Percentage Distribution of ^{65}Zn at Various Depths of Soil Column.

Each nutrient-treated soil specimen was thereafter leached with 500 ml. of redistilled water after the prementioned time gap. Leaching was tried at the beginning with 100 ml. of redistilled water at a time in 5 successive stages. Leachets were tested in each case by γ-counting for assessing the washed out nutrients. No recordable activity was noted on the leachets after 3 to 4 leachings i.e. after washing the soil column with 300 to 400 ml. of redistilled water. Fig. 3 depicts one such record for ^{65}Zn To be on the safe side, therefore, each nutrieted soil column was leached with 500 ml. of redistilled water and then it was put for the investigation.

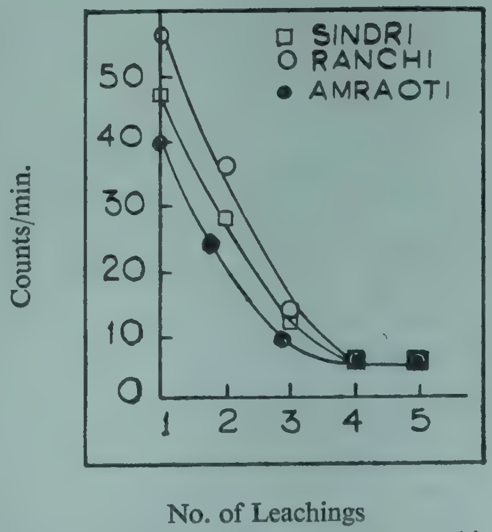

Fig. 3—Counts for ^{65}Zn in Leachets after Washing the Soil Column in Successive Stages. Each with 100 ml. Water.

Vertical distribution of tagged micronutrients in Sindri (pH 6.5), Ranchi (pH 4.9), and Amraoti (pH 8.5) soils are shown in Figs. 4, 5 and 6 respectively. It is marked that, according to their behaviour in soils taken, the micrountrients may be classified into two groups, viz. (i) iron, manganese and molybdenum and (ii) zinc and cobalt. The mobility of iron, manganese and molybdenum have been found similar and uniform. Their percentage distribution (D) in the vertical soil column falls sharply from the initial value up to a depth of 4 to 8 cm, after which it varies slowly and tends to reach a constant value. Thereafter, retentions of iron, manganese and molybdenum are much more within 4 to 8 cm of soil depth compared to that in the lower part covering 8 to 24 cm.

Unlike other micronutrients, the vertical distribution of zinc and cobalt have shown prominent peaks in every soil. Their percentage distribution (D) increases slowly with soil depth reaches the maximum around 4 cm., and then decreases sharply upto 10-12 cm. Thereafter, the value of 'D' remains almost constant up to the end of the soil column. Zinc and cobalt retention is, therefore, maximum around 4 cm below the soil surface. Moreover, the soil retentions of zinc and cobalt within the depth range 4-14 cm. are also found more as compared to those of iron, manganese and molybdenum. For the depth range 14 to 24 cm of soil column, the retentions of all the micronutrients, viz. iron, manganese, molybdenum, zinc and cobalt have been found to be almost equal.

The effect of changing the soil pH and nutrient concentration on the microelement mobility and retention have also been investigated with Sindri soil. The pH of Sindri soil was changed from 6.5 to 3.9 and 7.4 by the standard method and used for the experiment. Fig. 4 (a & b) shows the percentage distribution and retention of the micro-elements in Sindri soil of pH 3.9 and 7.4 respectively. The effect of concentration (C_n) variation of the applied micrountrients in Sindri soil (pH 6.5) have been presented in Fig. 4 for C_n, C_{2n} and C_{4n} respectively. 'C_n' corresponds to the micronutrient concentration originally used. It has been marked that neither the change of soil pH nor the variation of nutrient concentration can alter the overall nature of nutrient mobility in the soils investigated. But retention has been found to vary considerably with soil pH. Maximum soil retention of the microelements have been found in the neutral soil, whereas it is comparatively less both in acidic and alkaline soils. For Sindri soil, the retention of zinc, cobalt and other micronutrients have been found to be maximum at pH 6.1 (Fig. 4). But the retention was found less both at pH 3.9 and 7.4 (Fig. 4). It may be marked (Fig. 4) that there was hardly any effect on the nutrient retention when microelement concentrations of the added solutions were changed. This may be due to the fact that the initial concentration 'C_n' was enough for the maximum retention capacity of the amount of soil concerned. Therefore the increased concentrations 'C_{2n}' and 'C_{4n}' were of no use except the fact that the leachets contained more washed out nutrients at the beginning. The depths at which the percentage distributions 'D' of the retained micrountrients have been reduced to half, ($D_{1/2}$), in different experimental soils are shown in Table 2. The $D_{1/2}$ values indicate the soil depths after which the retained micronutrients will be less than 50 per cent of that added.

The vertical distribution of zinc and cobalt in soil showed prominent peaks at depths 4 to 6 cm. Similar findings were also reported earlier. Jurinak and Thorne[8] applied zinc as zinc chloride in silty clay loam. They observed that zinc was retained mostly at 3 cm. soil depth even when heavily leached. Brown *et al*[9] reported that mobility of zinc even when applied in the form of zinc sulphate or oxide was comparatively much low in sandy loam or silt loam soils. However, in contrast to this, Barrows, Neff and Gammon[10] observed that surface applied zinc sulphate was leached to a considerable depth in Lake land fine sand and Red bay fine sandy loam. But the downward movement of applied zinc was found inversely proportional to the soil content of phosphorus and organic matter and was also affected by the type and amount of clay minerals in the soil. Reaction of applied zinc with soil may also guide the zinc movement in soils of varying pH. Limited mobility of zinc in fine textured soils was also marked by Mortveldt and Giordano[11] when applied with various carriers. Benson[12] added 600 g. of zinc chloride tagged with ^{65}Zn to a previously wet soil column of 2 cm in diameter and 75 cm. along. He leached the column with 250 ml of redistilled water and observed that the surface 2.5 cm. of soil retained less zinc (3.9 mg. of Zn/g.) than the second increment at about 5 cm. depth (4.6 mg. of Zn/g.). Thereafter, a continued concentration of zinc with depth was found. According to Benson the peak of zinc retention was probably due to the competition of H-ions with zinc for a place on the exchange complex. Previous research[13] with the type of soils investigated presently indicated the exchangeable hydrogen is one of the important cations which were present in those. The zinc chloride solution was kept slightly acidic by hydrochloric acid and the H-ions reduced the zinc retained in the upper 2.5 cm. of soil. Increasing the ratio of hydrogen to zinc ions lengthened the zone of low zinc retention in the upper portion of the soil column and resulted in the so-called peak immediately thereafter. Since our results also corroborate the similar findings, all of the prementioned factors

TABLE 2—SOIL DEPTHS FOR '$D_{1/2}$' VALUES FOR MICRONUTRIENTS

	Sindri Soil			Ranchi Soil	Amraoti Soil
	pH 3.9	pH 6.1	pH 7.4	pH 4.9	pH 8.5
	Depth, cm.	Depth, cm.	Depth, cm.	Depth, cm.	Depth cm.
$D_{1/2}^{Fe}$	3.0	3.6	2.8	2.8	3.1
$D_{1/2}^{Mn}$	2.8	3.2	2.5	3.0	3.4
$D_{1/2}^{Mo}$	2.0	2.8	3.0	2.8	2.8
*$D_{1/2}^{Zn}$	11.2	7.8	9.8	9.6	8.6
*$D_{1/2}^{Co}$	9.5	8.2	9.0	9.4	8.6

*Soil depths for $D_{1/2}$ in the cases of Zn and Co have been measured from their peak positions in vertical distribution.

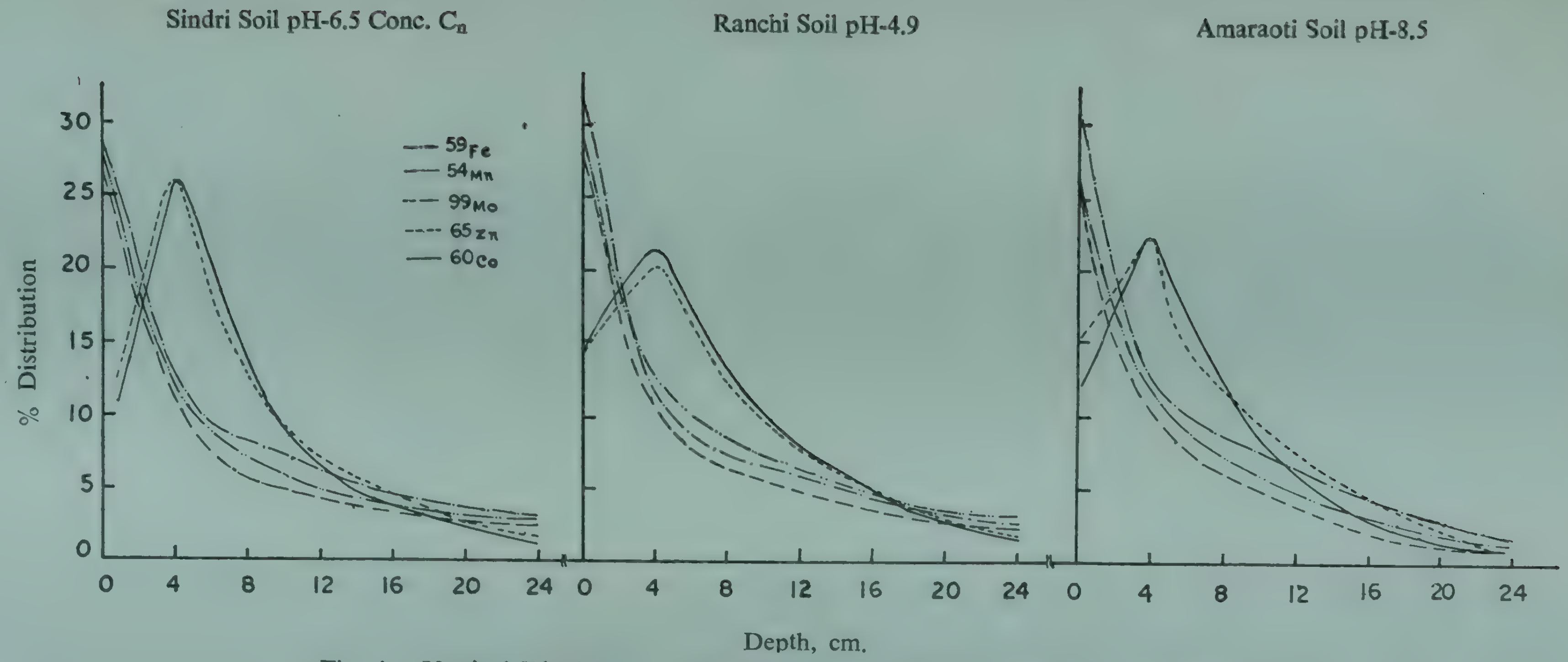

Fig. 4a—Vertical Distribution of Micronutrients in Sindri, Ranchi and Amaraoti Soils.

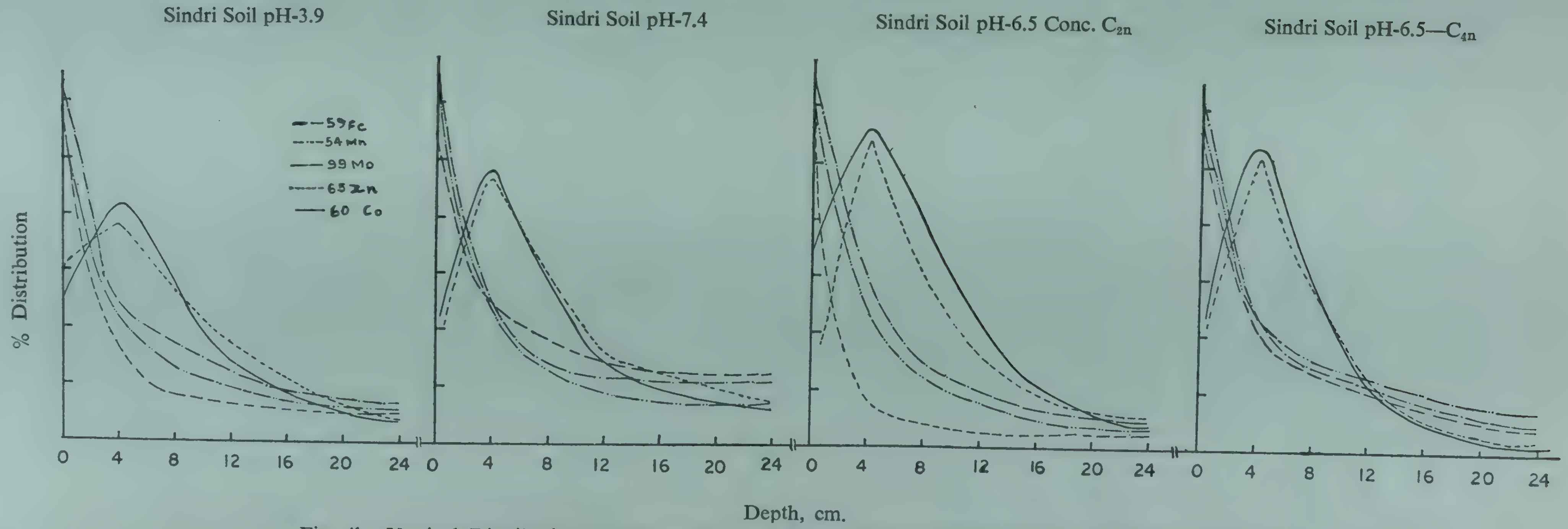

Fig. 4b—Vertical Distribution of Micronutrients in Sindri Soils at Different pH and Nutrient Concentrations.

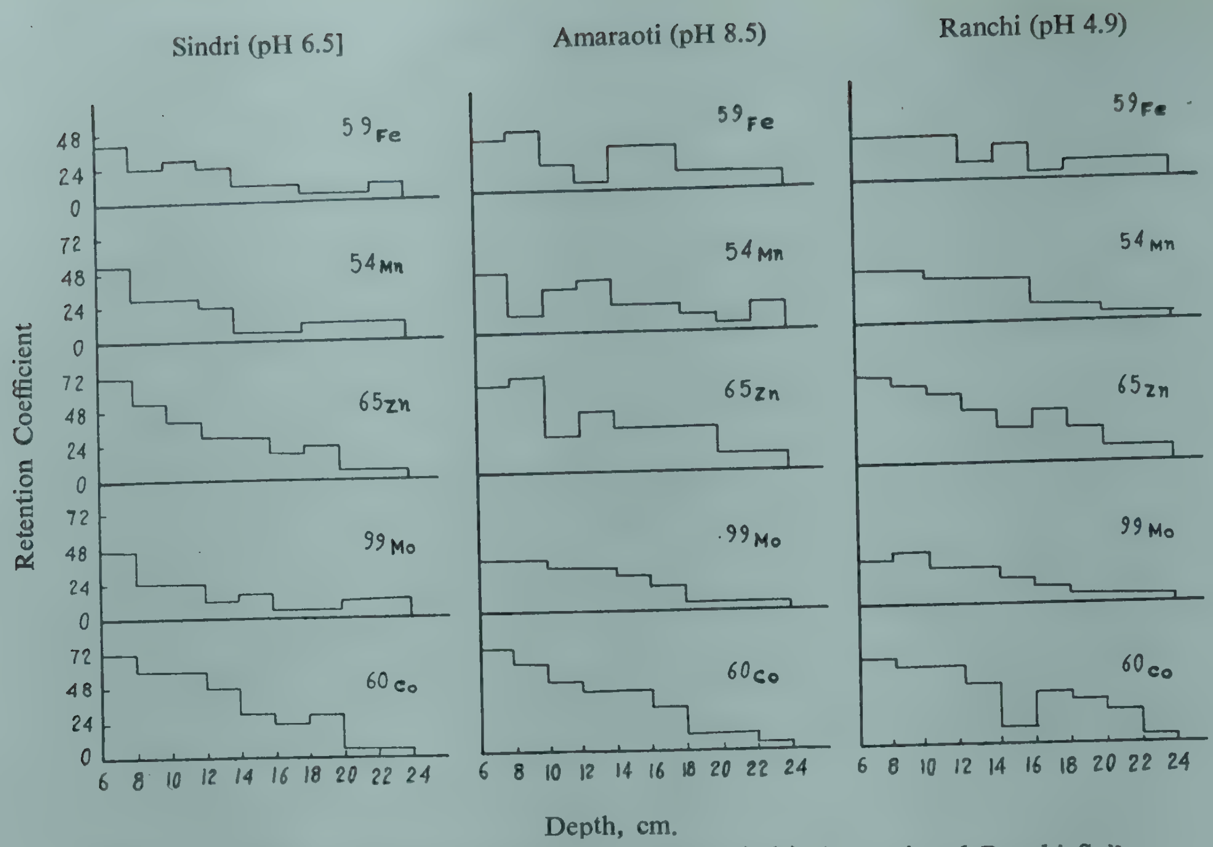

Fig. 5a—Retention Coefficient of Micronutrients in Sindri, Amraoti and Ranchi Soils.

might have also accordingly affected the mobility and retention of zinc in the present studies and contributed to the maximum retention at 4 to 6 cms depth in the vertical distribution patterns. However, specific adsorption of the element in the soil and its exchange characteristics with other soil elements also partially contribute to the maximum retention around certain depths forming the peak. Present investigation indicates that 'cobalt' also behaves almost similarly as zinc and maximum retention is around 4 cms of soil depth where it forms a prominent peak in its vertical distribution. This corroborates the earlier findings of Adams *et al*[14] and Tiller *et al*[15].

Above findings clearly indicate that the added micronutrients are retained mostly within the soil depth of 6 cm. or so. It has been found that variation of their retention in successive small vertical segments of the soil column is very small thereafter. The retention coefficients of the presently investigated soils have been calculated for individual micronutrient at specific depths by using the following relation:

$$r = \frac{q.d}{a},$$

where r = retention coefficient
q = percentage of nutrient retained
d = depth of soil segment
a = area of cross section of the soil column

The results have been presented in Fig 5 (as b).

In the present investigation, the micronutrients boron, copper and chlorine were not taken for the experiment. The first one was not available in a radioactive form. The available copper isotope, ^{64}Cu, is too short-lived (12.8 hr) for the present investigation and thus it was dropped. The third one, i.e. chlorine might have been used by tagging with ^{36}Cl. But ^{36}Cl being β-emitter, different experimental and counting set up was essential, which would be taken up later on.

An overall micronutrient deficiency has been marked in most of the Indian soils. However, iron is an exception. It is considered as a minor element in plant nutrition, though it can be taken as a macro-element in so far as its occurrence in soil is concerned. Total iron content in Indian soils varied between 0.46 to 26.3 per cent. But several interacting factors affect and limit the iron that plants can use. In Bihar soil, particularly Bikramganj area, which has been classified as a manganese deficient zone, the average total content of manganese is 800 to 1600 ppm[16,17]. Exchangeable manganese content in Punjab soil has been reported to be 0.1 to 3.4 ppm[3]. In black soil, manganese is less in available form, though the total content is comparatively high. Molybdenum is taken up by the plants in smallest quantity amongst the minor elements. The total and available molybdenum content in Indian soils ranges from 0.015 to 11.60 ppm, and traces to 1.65 ppm respectively. Almorah district in

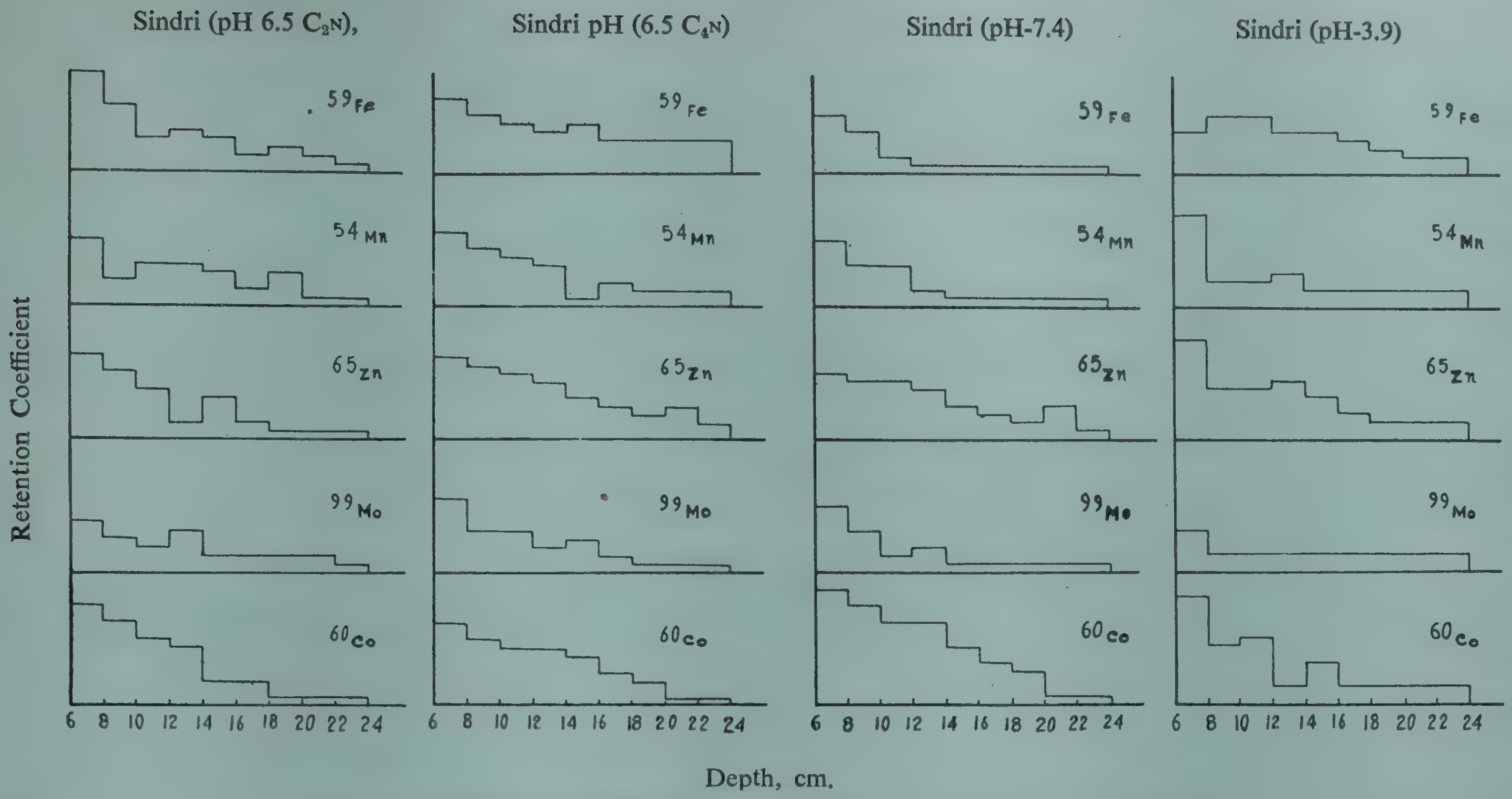

Fig. 5b—Retention Coefficient of Micronutrients in Sindri Soil at different pH and nutrient concentrations.

U.P. and several districts of Saurashtra region and Gujarat have particularly been reported deficient in molybdenum[18,19]. Zinc deficiency has been reported in many states, particularly Punjab, Haryana, U.P., Gujarat, Bihar, Andra Pradesh and Madhya Pradesh. Its deficiency in soil is mainly responsible to soil reactions, organic matter status, parent materials, cultural practice using heavy phosphatic fertilizers or timing etc. Total and available zinc content in Indian soils have been reported to be 14.4 to 86.9 ppm and 0.05 to 21.66 ppm respectively[21]. Zinc contents in red and black soils have been found to be 7 ppm and 1.1 to 3.8 ppm respectively[21]. U.P. soils are graded as deficient in cobalt where its available content varies between 0.22 to 0.24 ppm[22].

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[Original Mss. received on Dec. 12, 1972]

UDC 631.85: 631.42: 535.214

A radiotracer technique has been developed for rapid and accurate estimation of phosphate in rock phosphate and phosphatic fertilizer samples. The method involves precipitation of phosphate as ammonium phosphomolybdate using excess amount of molybdenum-99 tagged standard ammonium molybdate as the precipitant. The precipitate is separated by filtration and the unused activity accompanying the filtrate is assayed by counting a suitable aliquot in a well scintillation counter. The difference of the total activity added and that remaining in the filtrate readily gives the amount of ammonium molybdate consumed in precipitation and hence the phosphate content of the sample.

The present method combines accuracy and wide concentration-range applicability with speed—a feature unknown in any single procedure for phosphate estimation reported so far. A large number of samples with known as well as unknown phosphate contents have been analysed and the results compare very favourably with simultaneously carried out gravimetric analyses.

A Rapid Radio-Tracer Technique of Phosphate Estimation

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The estimation of phosphate content of rock phosphate, a basic raw material for phosphatic fertilizers, is of utmost importance. A number of methods have been reported for this purpose, which include colorimetry[1–4], atomic absorption spectrophotometry[5,6], flame emission technique[7,8], spectrofluorimetry[9–13], polarography[14], complexometry[15] and gravimetry[16,17]. Colorimetric methods utilize coloured compounds formed by partial reduction of heteropoly complexes via coordination of molybdate ions with phosphorus. Depending upon the reducing agent employed and the acid media chosen, a number of modifications have been adopted. However, the methods are useful only for the low phosphate-bearing materials (<2 per cent P_2O_5). Moreover, they have all been standardized with pure acidic systems, which are poor digesting media for phosphates. Besides, the intensity-dependence bears a complex relationship with the amounts of phosphorus, reductant and molybdate present in the system.

The atomic absorption and flame emission techniques are essentially ppm range tools, involving meticulous calibration with a large number of standards and manifold dilution of the test solution to reach the optimum range of observed linearity between absorption/emission intensity and concentration. The methods require pre-removal of cations by ion-exchangers and thereby become still more cumbersome. Polarographic estimations are relatively quick, but they also require comparison with a calibration curve covering a wide region of concentration and suffer from strong interference from chloride, if present over 0.2 per cent. Spectrofluorimetric analysis is lengthy and even with the latest modifications, it is suitable for submicrogram levels of phosphorus only. Indirect complexometric estimation, however, takes about 3 hr per sample, involving precipitation of phosphate as metallic ammonium phosphate followed by titration of the metal with EDTA.

By and large, the gravimetric methods constitute the most common and reliable technique for the determination of phosphate. The analytical procedure, comprising precipitation of orthophosphate as ammonium phosphomolybdate and/or magnesium ammonium phosphate hexahydrate depending upon the presence/absence of interfering elements, covers a large concentration range but has the disadvantage of being too lengthy and time-consuming.

The present studies have been undertaken with a view to evolving a procedure, which while retaining all the advantages of gravimetry affords a substantial slash in the time of analysis.

The underlying principle of the present method is the precipitation of phosphate as ammonium phosphomolybdate with an excess amount of Mo^{99}-tagged ammonium molybdate solution of known concentration. The precipitate is separated by filtration and the activity of the filtrate is assayed by counting a suitable aliquot in a well-scintillation counter. The difference of the total activity added in the form of the precipitant and that found in the filtrate gives the amount of ammonium molybdate consumed in the precipitation and hence the phosphate content of the sample.

EXPERIMENTAL

(i) Reagents

The chemicals used were of A.R. grade. The reagent solutions were prepared with distilled water except those used for titrimetric standardization of phosphate and prepared with triple distilled water.

The standard phosphate solution was obtained by diluting a known volume of 85 per cent phosphoric acid and titrating it with a standard alkali using methyl orange as the indicator. The standard ammonium molybdate solution (25 g./100 ml.) and magnesia reagent were prepared as given in literature[16]. A standard ammonium molybdate solution was labelled by adding to it 1 ml (20 μ Ci/ml.) of active ammonium molybdate (in ammonium hydroxide solution*) prior to making up its final volume. Mo^{99} is γ-active with energies in the range of 0.14—0.78 MeV and the half-life of 67 hr.

(ii) Sample Preparation

The rock phosphate was finely powdered, homogeneously mixed, sieved to obtain crystals in 80-100 mesh range, dried at 120°C and preserved in a desiccator over fused calcium chloride. For each run, 0.125 g. of the powder was digested according to the following procedures.

(iii) Digestion Procedures

(1) The sample was treated with 20 ml. of 1:3 nitric and hydrochloric acid mixture and heated on a steam bath for 30 min. The solution was cooled and filtered through a Whatman 42 filter paper to remove the insoluble impurities.

(2) The sample was mixed with 10 ml. of nitric acid (conc.) and heated on a hot plate for about 10 mins. when 30 ml. of 60 per cent perchloric acid was also added to it. The digestion was carried out till the appearance of dense white fumes, when the solution was cooled, diluted to 20 ml. and subjected to filtration as in (1).

(3) The material was digested and evaporated to dryness on a hot plate with 20 ml. 3:1 nitric and hydrochloric acids mixture. The dried mass was baked at 120°C for 30 min., cooled and subsequently dissolved in 10 ml. of nitric acid (conc.). The solution was warmed and filtered to separate indigested stuff as above.

(iv) Analytical Techniques

(A) *Radiotracer Method*: The filtrate obtained above was warmed to 60°C in a thermostated water-bath and 50 ml. of warm, active molybdate solution was added to it. The mixture was allowed to remain in the bath for 30 min, cooled and filtered through Whatman 42 filter paper. The precipitate was twice washed with 5 ml. portions of 2 per cent ammonium nitrate solution and the filtrate was raised to 100 ml.

(1) **Radio Assay**—5 ml. of the above filtrate was assayed in a 2″ × 1.75″ NaI (T1) well-scintillation counter coupled with a single channel pulse height analyser. The crystal-well measured 1.5″ deep and 0.7″ wide. Specimen activities were assessed in terms of counts per minute at the photopeak position for Mo^{99}. All the measurements were taken under identical conditions. The samples were counted long enough to have good statistics and usual corrections for background, decay and dilution, etc. were duly incorporated.

(2) **Calculations**—The precipitation of ammonium phosphomolybdate may be represented by the following ionic equation:

$$3NH_4^+ + PO_4^{3-} + 12MoO_3 + 3H_2O \longrightarrow (NH_4)_3\ PO_4 . 12MoO_3 . 3H_2O \qquad (1)$$

according to which

$$12MoO_3 \equiv PO_4^{3-} \qquad (2)$$

$$\equiv \tfrac{1}{2} P_2O_5, \text{ since } 2H_3PO_4 \rightarrow P_2O_5 + 3H_2O \qquad (3)$$

When expressed in terms of weight, expressions (2) and (3) imply,

$$1727.4 \text{ g. of } MoO_3 \equiv 94.975 \text{ g. of } PO_4^{3-} \equiv 70.97 \text{ g. of } P_2O_5 \qquad (4)$$

Since 50 ml. (the amount added for precipitation) of the standard ammonium molybdate solution contains 1.035 g. molybdenum trioxide, the amount of the latter consumed in precipitation

$$= \frac{(A-B)}{A} \times 1.035 \text{ g.} \qquad (5)$$

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*Supplied by B.A.R.C., Trombay.

where A stands for the activity (CPM) in 50 ml of standard ammonium molybdate solution and B for that in the filtrate.

From equations (4) and (5), the amount of P_2O_5 in 0.125 g. of an unknown sample will be

$$= \frac{A-B}{A}\left[\frac{1.035 \times 70.97 \times 100}{1727.4 \times 0.125}\right]\% \quad (6)$$

$$= \frac{A-B}{A} \times 34.02\% \quad (7)$$

$$= \frac{A-B}{A} \times K\%, \text{ where K equals 34.02} \quad (8)$$

(B) *Gravimetric Methods*: (1) **As Ammonium Phosphomolybdate**—From the filtrate obtained after digestion, phosphate was precipitated as ammonium phosphomolybdate by adding excess of *inactive* standard ammonium molybdate solution exactly in the same manner as in the radiotracer method described above. The precipitate was separated by filtration under suction through a weighed G-4 sintered glass crucible and washed with three 10 ml. portions of 2 per cent ammonium nitrate solution and subsequently with two 5 ml. portions of alcohol and ether respectively. The precipitate was finally dried at 280°C and weighed as $(NH_4)_3[PMo_{12}O_{40}]$.

(2) **As Magnesium Ammonium Phosphate Hexahydrate**—The phosphate was first precipitated as ammonium phosphomolybdate as described above. The precipitate was redissolved in ammonia dil and to this was added 2 g. of ammonium citrate (masking agent). The solution was rendered weakly acidic with controlled amount of hydrochloric acid conc. and was successively treated with 25 ml. of magnesia and an excess of ammonia (conc.). The latter, which was introduced slowly with constant stirring, produced a white precipitate of $MgNH_4PO_4 \cdot 6H_2O$. The solution was allowed to stand for 20 min. before filtering through G-4 sintered glass crucible. The precipitate was dissolved in N hydrochloric acid and reprecipitated using 0.5 g. of ammonium citrate and 5 ml. of magnesia. The precipitate was filtered through a weighed G-4 crucible, washed as in (1) and kept in a desiccator for 15 min. before weighing.

Results and Discussion

The radiotracer method was first tested with a set of standard phosphate solutions each containing 22.14 mg. of phosphate. The results (Table 1) show that the individual values lie within ± 1.1 per cent of the correct value suggesting that the method possesses high reproducibility.

TABLE 1—Test Results

Sl. No.	Amount of Phosphate Found, g.	Variation, %
1	22.04	−0.5
2	22.32	+0.8
3	21.90	−1.1
4	22.00	−0.6

Table 2 contains the results of the unknown samples. It is seen that with practically all the samples, the digestion with 3:1 nitric and hydrochloric acid mixture followed by 30 min. baking at 120°C, is the most efficient extractant of the three combinations used for the purpose. This may be due to complete elimination of flouride and organic substances in the present case, while in the other two their existence inhibits the process of precipitation. Similar views have been expressed by Peck[18] who recommends ignition of the sample for total decomposition of organic materials. The P_2O_5 yield determined by the radiotracer method is in good agreement with that obtained by the gravimetric methods. The unique advantage of the method is that it takes about 2 hr. as against 2 days needed for gravimetric estimations. This is because the radiotracer method concerns itself only with the filtrate and not the precipitate which is attendant with lengthy procedures of scrupulous drying and weighing till constant weight.

Another substantial cut in analysis time accrues from the fact that filtration succeeds precipitations only by 30 min. compared to overnight standing recommended for gravimetric methods. The above modification was effected upon studying the influence on the P_2O_5 yield of variation in the time-span for which the solution was allowed to stand (aging period) before filtration. The results with Kasipatnam rock phosphate sample are presented in Table 3.

It can be observed that, within the limits of experimental error, P_2O_5 yield is independent of aging between 0.5 and 12 hours and hence the solution need not stand overnight before subjecting it to filtration.

There has been some apprehension[19] regarding the uncertainty in the composition of ammonium phosphomolybdate precipitate. This is attributed to the conditions of precipitation. But recent studies[19] reveal that the uncertainty does not amount to more than 0.05 per cent in terms of P_2O_5 and hence can be safely ignored. In addition, the values of P_2O_5 determined by this method are in good agreement with those ending up with the precipitation of $Mg.NH_4PO_4.6H_2O$ which is devoid of any compositional doubt. This offers yet another proof of authenticity of the present method. The determinabi-

TABLE 2—RESULTS OF UNKNOWN SAMPLES

Sl. No.	Origin	DIGESTING MEDIA								
		HNO$_3$ & HCl 1 : 3			HNO$_3$ & HCl 1 : 3			HNO$_3$ & HCl 3 : 1		
		Percentage of P$_2$O$_5$								
		Radiotracer	Amm. Phos Molybdate	Mag. Amm. Phosphate	Radiotracer	Amm. Phos. Molybdate	Mag. Amm. Phosphate	Radiotracer	Amm. Phos. Molybdate	Mag. Amm. Phosphate
1.	A$_1$	21.8	21.1	21.4	25.5	25.2	26.7	25.4	27.2	26.9
2.	A$_2$	21.8	20.4	21.2	26.1	25.9	27.4	24.9	26.5	26.3
3.	J$_1$	19.7	19.7	17.6	10.1	17.3	16.6	23.0	25.2	24.5
4.	J$_2$	19.6	17.3	17.4	17.1	16.4	16.8	24.2	25.7	25.5
5.	Jh$_1$	25.5	24.3	23.4	23.0	25.8	24.4	21.7	23.8	23.4
6.	Jh$_2$	25.2	23.8	23.6	25.1	26.3	26.1	22.4	24.5	24.2
7	Jo$_1$	20.0	20.8	23.3	23.1	22.8	23.1	21.4	21.5	22.8
8.	Jo$_2$	21.9	20.8	22.6	21.7	23.0	23.4	22.5	21.7	22.4
9.	K$_1$	18.1	17.4	17.9	17.0	18.1	18.2	25.8	26.9	25.8
10.	K$_2$	16.6	16.3	17.2	15.9	17.8	17.2	26.4	26.9	26.9
11.	N$_1$	13.5	10.8	11.6	12.7	12.4	13.9	20.5	20.1	19.1
12.	N$_2$	13.7	11.7	10.4	13.7	12.7	12.7	20.7	20.3	19.5
13.	P$_1$	11.5	10.8	10.6	13.8	12.7	12.3	10.8	10.8	11.7
14.	P$_2$	12.2	11.6	11.9	14.1	12.4	12.4	10.6	11.4	11.4
15.	SA$_1$	17.7	15.8	17.0	18.7	18.5	18.8	17.1	17.6	18.1
16.	SA$_2$	17.4	16.8	18.1	19.2	17.5	18.5	18.5	16.6	17.2
17.	SB$_1$	15.9	14.8	16.0	13.3	17.2	16.2	16.0	17.3	15.0
18.	SB$_2$	16.6	15.6	15.9	16.2	15.7	15.3	14.7	16.9	16.6
19.	T$_1$	17.3	18.1	18.9	19.7	17.7	17.8	24.1	25.7	24.1
20.	T$_2$	18.4	18.4	18.0	19.9	19.3	19.4	23.4	25.5	24.1

*Followed by baking. A—Algiers; J—Jaisalmer; Jh—Jhamar Kotra; Jo—Jordan; K—Kasipatnam; N—Nainital, P—Phosphatic Fertilizer; SA—Suphala (18:18:9); SB—Suphala (15:15:15); T—Tiruchirapalli.

TABLE 3—P$_2$O$_5$ YIELD AGAINST AGING TIME

Aging Time, hr.	P$_2$O$_5$, %
0.5	25.0
1.0	25.5
4.0	24.8
8.0	25.0
12.0	25.4

lity limit of P$_2$O$_5$ (34%) inherent in (7) can be further extended by adding increased amount of the magnesia mixture.

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[Original mss. received on 30.11.72]

UDC547.495.2+546.273-37: 536.626

Differential calorimetric and gas evolution analysis of urea-orthoboric acid system have been carried out in the temperature range 50—180°C. A definite addition compound between two molecules of urea and one molecule of metaboric acid is found to form at 70°C. The heat of reaction is −9.56 KCal/mole. The effect of moisture on the system has been found out. It hinders the formation of such a compound.

Differential Scanning Calorimetric Study of Urea-Boric Acid System

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In fertilizer industry, boron is mainly used as a micronutrient. It is generally mixed in the soil along with urea, ammonium sulphate and various other nitrogenous and phosphatic fertilizers. In most of the cases, a mechanical mixture[1] of a boron-containing compound like boric acid or borate along with nitrogenous or phosphatic fertilizer is used. But very little is known on the interaction of nitrogenous fertilizers with boron oxides and acids. Recently, Skvortsov *et al*[2–4] have reported an addition compound of urea with orthoboric acid but its physico-chemical properties have not been studied in detail.

It would therefore be interesting to know their detailed physico-chemical characteristics, like stability, nature of compound formation, if there is any, their probable composition, mechanism of reaction, energies of such reactions and the effect of moisture and pressure on such reactions.

In order to throw some light on the above properties, precise thermal studies have been undertaken. In the present investigation, only urea-boric acid system has been studied.

Experimental

Samples used for this investigation were prepared from A.R. quality ingredients, which were preserved before use in a desiccator using calcium chloride as the dehydrating agent. Binary mixtures containing 100, 95, 80, 75, 67, 50, 20, 10 and 5 molar per cent of urea with rest of orthoboric acid were prepared mechanically in an agate mortar and subjected to thermal analysis.

The differential calorimetric study of all these samples and the individual components were performed in a differential scanning calorimeter* in the temperature range 50-180°C. The heating rate was 8°C/min. The samples were taken in standard aluminium pans which were sealed by means of a crimping device so as to withstand a pressure of 30 psi. During the experiment, a dynamic nitrogen atmosphere was maintained in the reaction chamber. A sample quantity (2-5 mg.) was sufficient which was used in the powder form. A similar empty aluminium pan was used as the reference material.

The energies associated with the reactions were calculated from the areas of the thermograms as measured with the help of a planimeter. Metallic tin was used as an external standard because it has a well-known transition energy (Latent heat of fusion = 14.5 Cal/g.) in the experimental temperature range and is available in high purity. The following equation was used for energy calculation.

$$H_{(m)} = \frac{H_{(T)} \times S_{(m)} \times W_{(T)}}{S_{(T)} \times W_{(m)}},$$

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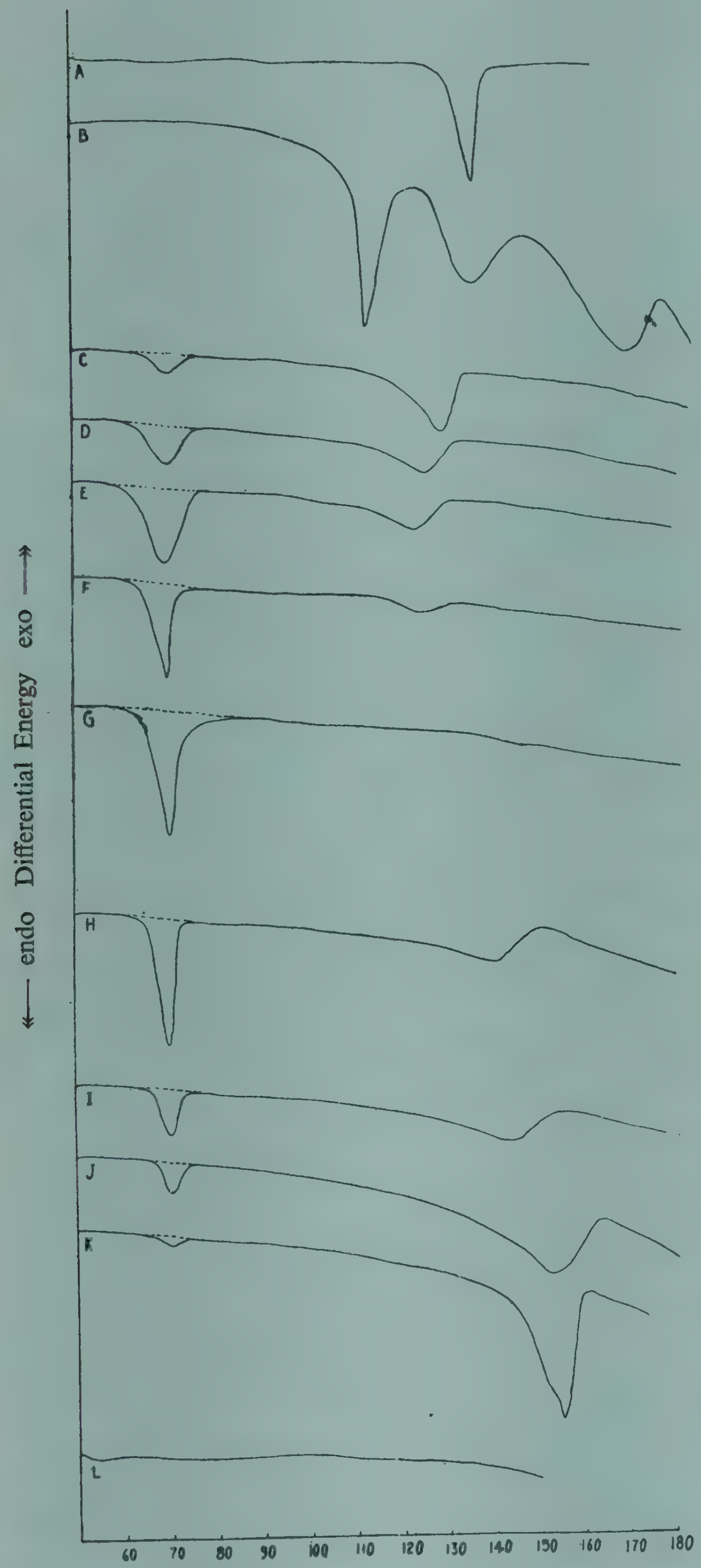
*Perkin–Elmer DSC-IB.

where

$H_{(T)}$ = Heat of fusion of tin
$S_{(m)}$ = Area of the transition peak of the mixture
$S_{(T)}$ = Area of the transition peak of tin
$W_{(T)}$ = Weight of tin
$W_{(m)}$ = Weight of the mixture



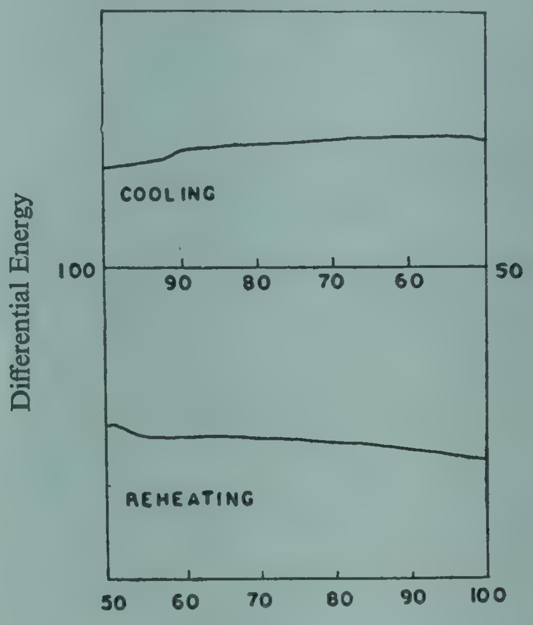
Temp., °C
Fig. 1—Calorimetric Studies.

The energy of formation of the proposed compound was also calculated theoretically for all the mixtures from a single energy data obtained for the mixture 67:33 mole per cent urea: boric acid, where hundred per cent conversion took place.

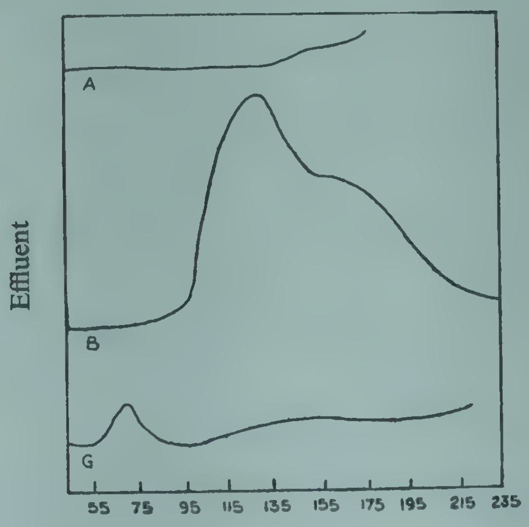
The gas evolution analyses of urea, orthoboric acid and a mixture of specific composition (2:1) were carried out with the same instrument. In all cases, open sample pans were used and the carrier gas was dry nitrogen.

Calorimetric studies are presented in the Fig. 1. Fig. 2 shows the cooling and reheating curves of 2:1 sample and Fig. 3 shows the curves of gas evolution analysis.

Table 1 shows the observed energies in Cal/g. of the sample, while Table 2 the comparison between theoretical



Temp., °C
Fig. 2—Cooling and Reheating Curves of 2:1 Mixture.



Temp., °C
Fig. 3—Gas Evolution Analysis.

and observed energies. Peak temperatures are given in Table 3 and sample quantities in Table 4.

TABLE 1—OBSERVED ENERGIES FROM DIFFERENTIAL CALORIMETRIC CURVES

Sample Designation	Composition of Urea: Boric Acid, mole %	Energy at 70°C of Sample, cal./g.
A	100:0	—
B	0:100	—
C	95:5	− 9.0
D	90:10	−15.5
E	80:20	−30.9
F	75:25	−38.4
G	67:33	−53.0
H	50:50	−39.6
I	20:80	−15.2
J	10:90	−8.38
K	5:95	− 3.5

TABLE 2—COMPARISON OF CALCULATED AND OBSERVED ENERGIES

Sample Designation	Calculated Energy, cal./g.	Observed Energy, cal./g.
G	—	−53.0
C	− 7.95	− 9.0
D	−15.9	−15.5
E	−31.8	−31.1
F	−39.8	−38.4
H	−39.8	−39.6
I	−15.9	−15.2
J	− 7.95	− 8.33
K	− 3.98	− 3.5

TABLE 3—PEAK TEMPERATURE OF THE THERMOGRAMS

Sample Designation	Peak Temperature, °C	
	Calorimetric Study	Effluent Study
A	136	—
B	114,136,169	130,175 (hump)
C	70,129	—
D	70,126	—
E	70,124	—
F	70,124	—
G	70,—	70
H	70,140	—
I	+ 70,144	—
J	70,152	—
K	70,155	—
*L	—	—

*Sample with added moisture

TABLE 4—SAMPLE WEIGHTS FOR CALORIMETRIC STUDY

Sample Designaion	Sample Composition of Urea: Boric Acid, mole %	Sample Weight, g.
A	100:0	—
B	0:100	—
C	95:5	0.0030
D	90:10	0.0045
E	80:20	0.0045
F	75:25	0.0025
G	67:33	0.0030
H	50:50	0.0028
I	20:80	0.0027
J	10:90	0.0030
K	5:95	0.0020
**L	67:33	0.0035

**Sample with added moisture

Results and Discussion

In Fig. 1 the curves A and B represent the thermograms of pure urea and orthoboric acid respectively. The single endothermic peak at 136°C in the curve A is due to the melting of urea. In the curve B three successive endothermic peaks at 114, 136 and 169°C are due to the transformation of orthoboric acid to metaboric, pyroboric and finally B_2O_3 respectively. All such transformations are reported in the literature[5,6]. Recently DTA studies of boric acid have been made by Marano *et al*[7]. They have also found peaks for all such transformations. Unlike that of the pure components, a new peak at 70°C (Fig. 1) appears in the thermograms of all the mechanical mixtures of urea and boric acid and the intensity of the peak corresponding to 2:1 molar composition of urea: boric acid is maximum. But in mixtures where urea is higher than this optimum binary composition a second endothermic peak around 129-124°C (Fig. 1, curves C to F) appears and in mixtures having boric acid higher than this composition this peak appears at 140-155°C. It is interesting to note that this second peak is totally absent in the thermogram of a mixture having this optimum composition, viz. 2:1 (urea: boric acid). Moreover, the energy of the peak at 70°C of the mixture of 2:1 molar composition is highest and it decreases uniformly when urea content increases or decreases beyond this stoichiometric composition. Earlier workers reported an adduct formation between two molar proportion of urea and one molar proportion of boric acid at 60°C. Our experimental results indicate such an adduct is formed at 70°C. The sample containing 2:1 molar ratio was subjected to gas evolution analysis and peak due to evolution of water has been observed exactly at 70°C. It seems that during the reaction between urea and boric acid one molecule of water is removed and a compound is formed between urea and metaboric acid which may be represented as follows.

$$H_3BO_3 + 2NH_2CONH_2 \longrightarrow (NH_2CONH_2)_2.\ HBO_2 + H_2O$$

Incidentally, it can be mentioned here that pure boric acid transforms into metaboric acid with the elimination of one molecule of water at 114°C (curve B, Fig. 1).

The heat of reaction calculated from observed energy data is found to be -9.56 KCal/mole. The low order of magnitude of heat of reaction indicates a weak type of bonding which is quite probable in the case of an addition compound. Further, the energies calculated theoretically for all the mixtures are in excellent agreement (Table 2) with their observed data. This confirms that a definite compound having the formula $(NH_2CONH_2)_2.HBO_2$ is formed in all the mixtures at 70°C under the experimental condition. The compound is definitely an addition compound of urea and metaboric acid and not with orthoboric acid, as indicated by Skvortsov *et al*[4].

It has been further noted that when moisture was introduced in the system the effect at 70°C in the thermogram is lost (curve L, Fig. 1). This confirms the view that the compound is formed through elimination of water.

The process of formation of the compound is irreversible as it is evident that the mixture does not give any similar peak on cooling or reheating (Fig. 2). It may be pointed out, however, that the second peak which appears either at 124-129°C or 140-155°C is due to melting of free urea or final transformation of boric acid respectively. But this change occurs at relatively lower temperature than that of their individual constituents. This lowering may possibly be due to formation of a new compound as a result of solid-solid interaction along with the elimination of water.

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[Original mss. received on March 31, 1973]

UDC 546.881: 541.67: 547.587.11

A complex of vanadium (IV) with 5,5′ thiodisalicylic acid has been prepared. The isolated complex has the composition 1:1 M:L and has been characterized by elemental analysis, magnetic susceptibility measurements, e.s.r., i.r. and absorption spectral studies. The anomalous magnetic behaviour has been explained on the basis of metal-metal interaction. The two chelating sites contained in the ligand molecule have been taken to coordinate separately, giving rise to a polymeric structure.

Anomalous Magnetic Behaviour of Vanadium (IV) Complex with 5,5′ Thiodisalicylic Acid

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Introduction

Recently, much interest has been shown by several workers on anomalous magnetic behaviour of vanadium (IV) complexes[1–3]. 5,5′ thiodisalicylic acid $[C_6H_3(COOH)(OH)]_2S$, an industrially important compound[4], has been used as a complexing agent and its reactions with transition metal ions have been studied[5–10]. It forms complexes of polymeric nature having mostly subnormal magnetic behaviour. Due to the anomalous nature of vanadium (IV) complex with 5,5′ thiodisalicylic acid, it was of interest to study the magnetic properties of the complex in detail. In this paper, the magnetic properties e. s. r., infrared and electronic spectral data of the complex have been reported. [5,5′ thiodisalicylic acid is hereafter abbreviated as TDSA.]

Experimental

Preparation: The ethanolic solution of TDSA (0.1 mol.) was added to the vanadyl chloride solution in absolute alcohol (0.1 mol. was dissolved in 100 ml.). The pH of the solution mixture was found to be 3.2. The solution was refluxed on a water-bath for 1 hour. The separated precipitate was washed several times with absolute alcohol and finally with acetone and dried in an oven at 60°C. The yield was about 70 per cent. The complex is yellow green in colour, and insoluble in common solvents. It decomposes above 280°C. The elemental analysis of the complex showed it to be $VO(C_{14}H_8O_6S)2H_2O$ which requires since it is constituted of V = 12.03, S = 8.02, C = 41.20 and H = 3.06 per cent as against the theoretical amounts V = 12.53, S = 7.86, C = 41.27 and H = 2.94 per cent.

Analysis: The analysis of the complex for carbon and hydrogen contents was done at the Micro-analytical Section of the Indian Institute of Technology, Kanpur.

Physical Measurements: Magnetic measurements at room and other temperatures and on the solid complex were made with Guoy's balance.

The e. s. r. spectra of the complex were recorded on an x-band spectrometer from Brucker-Physik A. G. (model B-ER 402), using a TE_{102} mode rectangular cavity. The magnetic field was measured by a proton resonance gaussmeter and the g values using polycrystalline DPPH as reference (g = 2.0036).

The absorption spectra of the complex were recorded with a Cary Spectrophotometer Model 14 provided with an automatic recording system. The spectra were taken in nujol mull.

Infrared spectra of TDSA and its complex were recorded on a Perkin-Elmer recording Spectrophotometer Model 521 fitted with NaCl and KBr optics in the range of 4000 to 250 cm^{-1}.

Results and Discussion

Vanadium has electronic configuration [A] $3d^3$, $4s^2$, therefore V (IV) has the electronic configuration $3d^1$. The magnetic moment values of the complex are in the range 0.42—1.32 BM between 90 and 300°K. Evidently the room temperature μ_{eff} value of the compound is lower than spin only value (1.73 BM) expected for d^1 system. From Table 1, it is clear that magnetic moment of the complex decreases considerably as the temperature is lowered. The dependence of magnetic susceptibility on temperature of the complex is characteristic of exchange coupled antiferromagnetism.[1] A plot of χ_M corr. vs T (χ_M corr. molar susceptibility against diamagnetic corrections) curve (Fig. 1) clearly indicates of the abnormality. The exchange integral J was calculated using Bleaney and Bower's equation[11] and found to be 280 cm^{-1}. The J value is known to correspond to separation between the singlet and triplet states and becomes a guiding factor in discussing magnetic interaction. The greater magnetic interaction at lower temperature in the complex, as evidence by χ_{M-T} plot, perhaps arises from the possibility of polymeric nature of the complex and presence of some metal-metal interaction[12]. The copper (II) with 5,5′ thiodisalicylic acid exhibits subnormal magnetic moment and has been shown to have polymeric structure. The unpaired electron is in the $d_{x^2-y^2}$ orbital and electronic spin-spin coupling takes place by the super exchange interaction[9]. In the present vanadium (IV) complex, the unpaired electron is in the d_{xy} orbital and the overlap of d_{xy} orbitals of the adjacent vanadium atoms leads to direct spin-spin coupling with metal-metal interaction. As the complex is insoluble in common solvents, its e. s. r. spectra were recorded in the poly-crystalline sample and analysed according to the standard procedure,[13,14] wherefrom parameters were calculated as given below:

Compound	g II	g I	D cm.$^{-1}$
$VO(C_{14}H_8O_6S)2H_2O$	1.90 ± 0.02	1.99 ± 0.02	0.050

TABLE 1—MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Complex	Temperature, °K	$M,^{corr}, \times 10^6$ C.G.S.	μ_{eff} (B.M)
$VO(C_{14}H_8O_6S)2H_2O$	296	740.4	1.32
	250	724.7	1.20
	230	661.9	1.10
	190	400.5	0.78
	155	342.9	0.65
	125	282.7	0.53
	110	263.4	0.48
	90	246.1	0.42

TABLE 2—ELECTRONIC SPECTRAL DATA

	Position of Bands	Assignments
$VO(C_{14}H_8O_6S)2H_2O$	13,720 cm.$^{-1}$ (w)	$d_{yz}, d_{xz} \leftarrow d_{xy}$
	15,000 cm.$^{-1}$ (sh)	$d_{x^2-y^2} \leftarrow d_{xy}$
	20,300 cm.$^{-1}$ (w)	$d_{z^2} \leftarrow d_{xy}$

w = weak　　sh = shoulder

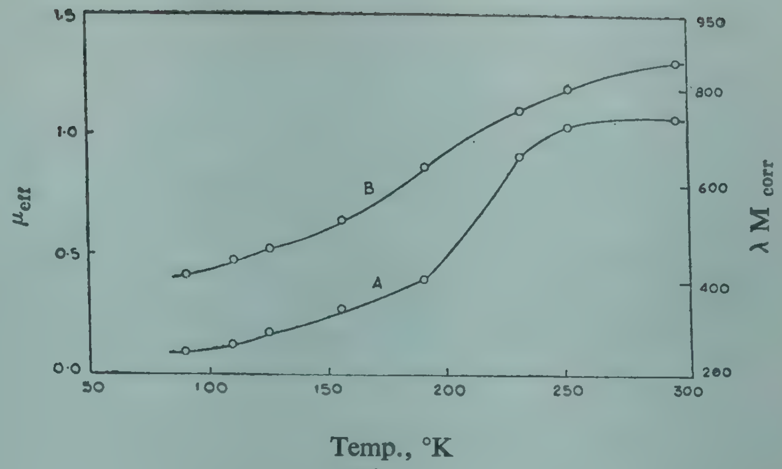

Fig. 1

The electronic spectra of the complex exhibits three weak bands arround 13,720, 15,000 and 20,300 cm^{-1}. The assignment of the electronic spectral bands of the vanadium (IV) complexes has been a matter of controversy. Here, it has been made on the basis of the scheme of Vanquickenborne and Mcglynn[15], who have proposed a new energy level diagram by reconsidering Ballhausen-Gray[16] and Ortolano-Selbin-McGlynn[17] schemes. The following ordering of vanadium (IV) d orbitals have been proposed: $d_{xy} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$. According to the above scheme the folowing assignments are made.

13,720 cm^{-1}	d_{yz},	$d_{xz} \longleftarrow d_{xy}$
15,000 cm^{-1}	$d_{x^2-y^2}$	$\longleftarrow d_{xy}$
20,300 cm^{-1}	d_{z^2}	$\longleftarrow d_{xy}$

The position of the infrared bands attributed to the carboxylic group as compared with those in the ligand suggest unidentate co-ordination of these groups[8-10]. The absorption bands of diagnostic value and their tentative assignments are given in Table 3. The new bands also arise in the region 400-500 cm^{-1}.

TABLE 3—I. R. SPECTRAL DATA OF THE COMPLEX

Compounds	$\nu_{asym}C < \substack{0\\0}$	$\nu_{sym}C < \substack{0\\0}$	$\delta C < \substack{0\\0} + \nu C\text{-}0$	$\nu M\text{-}0$ *
$C_{14}H_{10}0_6S$	1660	1600	1200	—
$VO(C_{14},H_8O_6S)\ 2H_2O$	1540	1600	1130	410

*In dikitonates a band at this region contains a substantial contribution from metal-oxygen stretching. [Nakamoto, K., *Infra-red Spectra of Inorganic and Co-ordination Compounds* (John Wiley and Sons, Inc., N. Y.), 1962].

The two chelating sites in the ligand molecule perhaps co-ordinate giving rise to polymerization.

Acknowledgement

The author is thankful to Dr. H. L. Nigam, Department of Chemistry, Allahabad University, Allahabad and to Dr. B. K. Banerjee, Superintendent, Physical Research Wing, P and D Division FCI Ltd. for valuable discussions and interest in the topic.

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[Original mss. reeived on Sept. 15, 1973]

UDC 541.128: 546.74–31+546–621: 542.941

The basic requirements for a catalyst are its activity, stabilty, life and specificity. These requisite qualities are to a great extent dependent on the heterogeneity of the catalyst surface. The results of the present investigation indicate that kinetics of reduction of supported nickel oxide-alumina type catalyst can be used to evaluate the degree of heterogeneity.

It has been observed that systems identical in chemical and phase compositions may have different degrees of heterogeneity, and such differences originate from the variations in the mode of preparation. Kinetic studies have been based on the applicability of different rate equations to the reduction process. On the basis of the Elovich equation which has been found to fit the data obtained with impregnated catalyst only, it is concluded that the degree of heterogeneity is much pronounced in this catalyst.

Kinetics of Reduction of Nickel Oxide-Alumina Type Catalyst—An Assessment of Heterogeneity of Surface*

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Introduction

The interaction between the carrier and a catalytic metal in a system, similar to the one studied, results in energetically different surface sites, which can influence the activity and selectivity of the catalyst to different extents. This heterogeneity of surface sites has been demonstrated in a number of investigations by Maxted[1–2], Baddour[3], Taylor[4–5] and Solymosi[6], using a variety of catalysts, supports and reactions.

Nickel as the active catalyst component has wide commercial use for many industrial reactions. The refractory-type supports, like alumina, make the catalyst suitable for wide range of temperatures. The selectivity of nickel oxide-alumina system has wide application in various processes, and reformation of hydrocarbons may be considered as a typical example. It is known that a number of side reactions along with carbon liberation and gasification are possible. Selectivity and specificity of sites for carbon gasification is one of the most important contributing factors for ultimate stability of reformation catalysts.

Several techniques, such as chemisorption[7], and selective poisoning by hydrogen sulphide using a pulse reactor[8], have been employed for evaluation of surface heterogeneity. Hydrogen reduction studies have also been used by many authors[9–13] for determining the degree of metal dispersion. Besides the evaluation of heterogeneity, the study of reduction rates and mechanism helps in the formulation of the correct operation at stages for the activation of catalyst in commercial units.

In the present investigation the heterogeneity of the catalysts has been assessed in a comparative study of two samples of nickel oxide-alumina, prepared by impregnation and coprecipitation methods. The study also includes reduction of NiO. The assessment is based on the kinetic studies with respect to applicability of different rate equations to the hydrogen reduction process.

EXPERIMENTAL

Sample Preparation

Catalyst 1 (Unsupported NiO): Ammonia and carbon dioxide were added to a solution of nickel nitrate and the resultant nickel carbonate was washed, dried and calcined at 800°C.

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*Paper presented at the seminar on Catalysts in Chemical Industry held at I.I.T. Kanpur on the occasion of the 24th Annual Meeting of the Indian Institute of Chemical Engineers on February 26, 1972.

Catalyst 2 (Impregnated): Calcined alumina in the form of extruded rods were soaked in a solution of nickel nitrate. The sample was oven-dried and calcined till the complete decomposition of the nitrate, and soaking procedure was repeated till a nickel build-up of 8.6 per cent was achieved.

Catalyst 3 (Coprecipitated): From a mixed nitrate solution of nickel and aluminium, the respective metal carbonates were coprecipitated by adding ammonia and carbon dioxide. The precipitate was dried and calcined at 800°C. The finished product in the form of extruded rods contained 8.2 per cent nickel.

Hydrogen Reduction: Reduction studies were made in a Stanton Mass Flow thermobalance with a sensitivity of 0.2 mg. division. The gas flow rates were 2.5 l./hr. The other details are similar to as described earlier[14].

Phase Composition: Phase analysis as carried out by x-ray diffraction techniques for the supported catalysts (2 and 3) was same and is as follows:

Major phases —αAl_1O_3, $Ni\ Al_2O_4$
Minor phases —NiO, γ-Al_2O_3
Traces —Quartz.

Results and Discussion

(a) *Reduction of Unsupported Nickel Oxide*: A typical plot of percentage of reduction at time t is shown in Fig. 1. It can be seen that under the experimental conditions employed, the induction period is not very much pronounced, though the rates are comparatively slower for initial 7-8 min. and then attains its maximum velocity (Fig. 1).

The comparatively slower rates in the first step at the initial stages of reduction (7-8 min.) as in Fig. 1 may be treated as induction period and attributed to the nuclei formation during this period. The rates can be suitably expressed by equation

$$x^{1/2} = Kt \qquad (1)$$

where x is the fraction reduced in time t. This is evident from Fig. 1 where a plot of $\sqrt{x}$ vs t is linear up to 8 min. of reduction period.

The rate in the second step is accelerated and corresponds to the rate of metal-oxide interface progression. The equation which suitably describes the rate in this region is

$$\log \frac{x}{1-x} = Kt + C \qquad (2)$$

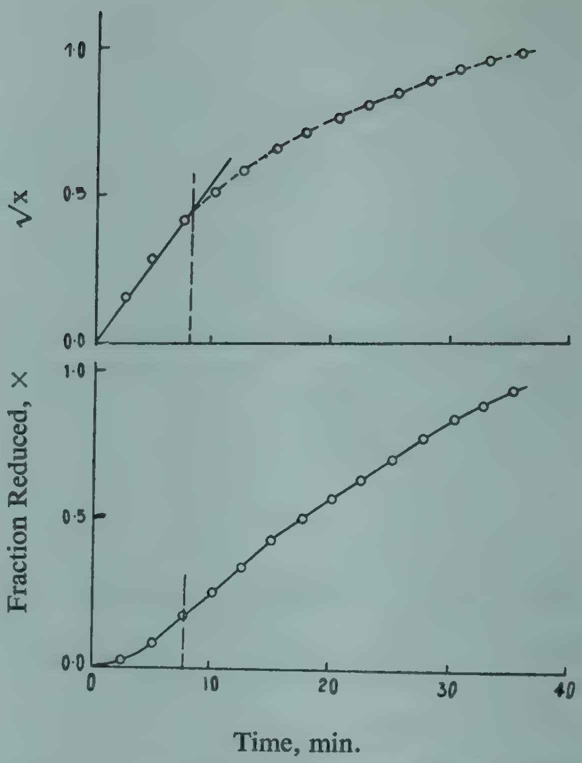

Fig. 1—Reduction of Unsupported Nickel Oxide (Catalyst 1) at 350°C.

A plot of $\log \frac{x}{1-x}$ against t in accelerated region is linear as seen in Fig. 2. Activation energy for the reduction has been calculated from an Arrhenius plot, which is equal to 3.5 k.cal/mole in the temperature range of 350-450°C.

The reduction of unsupported nickel oxide results in the formation of nickel crystallites of the order 600-700Å.

(b) *Reduction of Supported Catalyst*: It has been shown by several authors[9-13] that the methods of preparation of the supported catalyst have a great effect on the structure of the catalyst, and different preparation of nickel oxides on support are known to behave differently towards hydrogen reduction.

The typical reduction curves for catalysts 2 and 3 at two different temperatures, viz. 400 and 700°C, are shown in Fig. 3. The reactions are obviously much faster at higher temperature. In all the reduction curves, it can be seen that after the initial fast reduction the rate slows down considerably. The nature of reduction curves for supported catalyst shown (Fig. 3) is entirely different from that of the unsupported nickel oxide (Fig. 1), which implies a different mechanism of reduction. That the reduction mechanism is different for the supported nickel oxide is also clear from the fact that the first order equation 2 does not yield a linear relationship for the supported catalysts.

The differences in kinetics and mechanism of reduction of the supported and unsupported catalysts is not un-

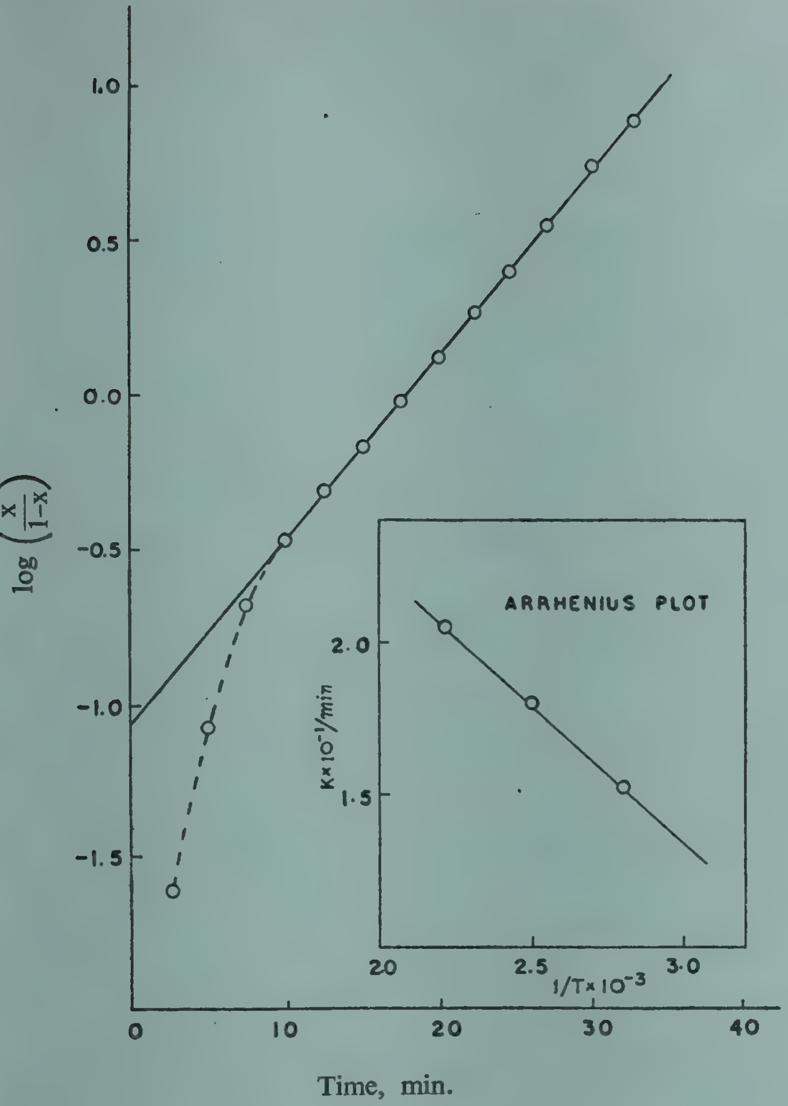

Fig. 2—Reduction of Unsupported Nickel Oxide (Catalyst 1) at 350°C.

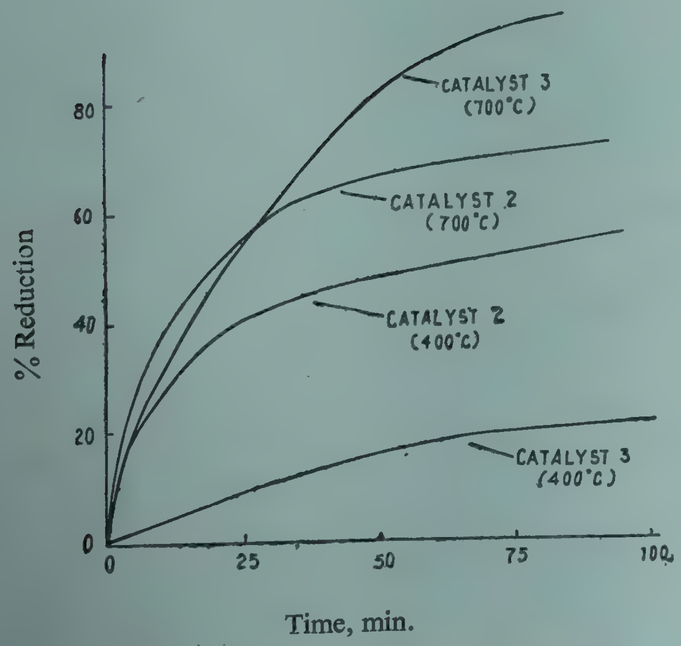

Fig. 3—Reduction of Supported Catalysts.

expected. In the case of supported catalysts, alumina acting as a spacer or barrier between the two nickel sites may resist the crystallite growth. That the crystallite growth arrest in supported catalysts occurs is clearly seen from the fact that the size of nickel crystallites in the supported catalysts is in much smaller range of 100-250Å as compared to 600-700°C in case of unsupported one.

Since it was understood that neither of the two equations used in the case of pure nickel oxide are applicable in the nickel oxide-alumina system, an attempt was made to test the applicability of other equations which have been used earlier by different authors[15–18] for kinetic studies of reduction process.

In consideration of the view that the rate controlling factor is the rate of reaction at the interface and progressive advance of the interface, a fractional order rate equation was considered. This type of equation has been used earlier for the reduction of mixed $NiO + ZnO$[15] and Fe_2O_3[16]. The equation is

$$1-(1-x)^{1/3} = Kt \qquad (3)$$

where x is the fraction reduced at time t. A linear plot of $(1-x)^{1/3}$ against t should indicate the applicability of this equation. The results for catalysts 2 and 3 obtained at 700°C, were plotted accordingly. It can be seen (Fig. 4) that a straight line results only with the coprecipitated catalyst (No. 3). The activation energy of the process has been calculated from an Arrhenius plot, equal to 14.4 K. cal/mole.

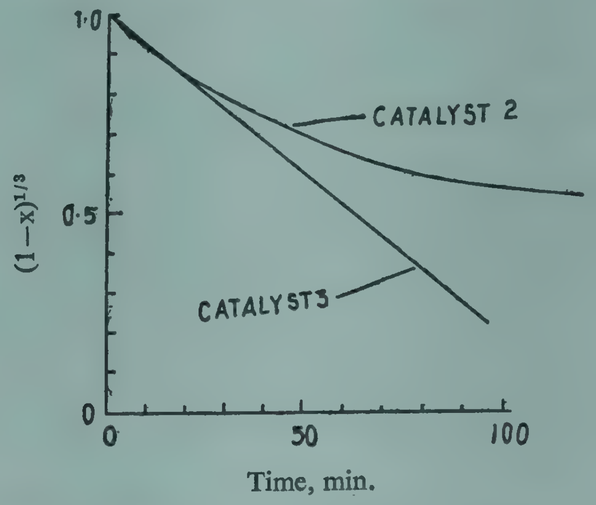

Fig. 4—Reduction of Supported Catalysts.

The reason for this different behaviour of catalysts 2 and 3 is likely to be due to the different dispersion and distribution of nickel on support.

An empirical equation has been derived for such reduction process which is,

$$\frac{x}{1-x} = Kt^n \qquad (4)$$

where

x is the fraction reduced
K is a constant
$n \geqslant 1$

The data for catalysts 2 and 3 have been plotted according to the above equation and are shown in Fig. 5. A straight line results only for catalyst (No. 2) which is impregnated catalyst, again indicating dissimilarities in kinetics behaviour of these two types of catalyst under discussion. For catalyst (No. 2) which follows above equation, the activation energy of reduction has been calculated, equal to 8.61 K.cal/mole.

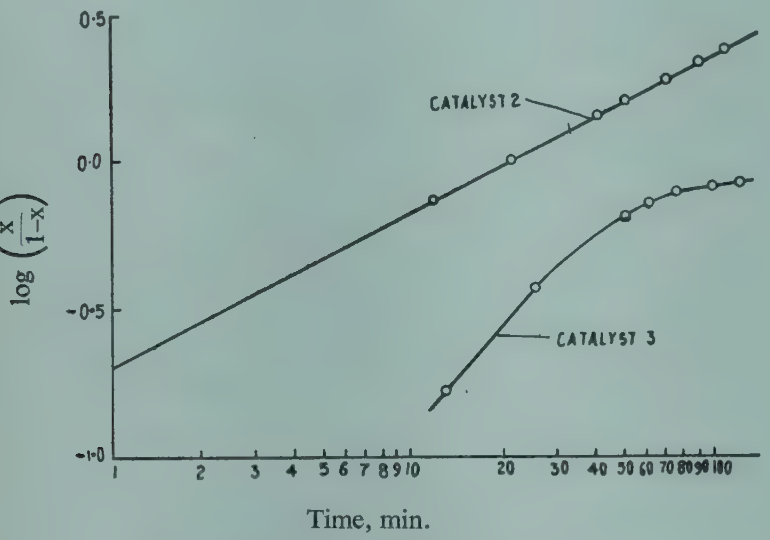

Fig. 5—Reduction of Supported Catalysts.

Lavinson[17] and Bicek[18] have used Elovich equation to describe the reduction process in supported nickel catalyst. Elovich equation may be written as

$$\frac{dx}{dt} = ae^{-bx} \qquad (5)$$

where x is the fraction reduced and 'a' and 'b' are empirical constants. The constant 'a' is independent of x and applies to rate process on heterogeneous surface, while 'b' is related to the spread in the activation energy during the course of reaction.

A linear plot of x vs log t indicates that the Elovich equation can be used to describe the particular reaction process. For both the catalysts 2 and 3, the plots are shown in Fig. 6. Here also only in the case of catalyst 2, a straight line is obtained indicating that Elovich kinetics are obeyed only in the impregnated catalysts. Where the Elovich kinetics are followed the activation energy should be a linear function of the rate of reaction. According to Dorer[19], the apparent energy of activation as a function of extent of reaction can be calculated as follows:

$$\text{Rate} = \frac{dx}{dt} = ae^{-bx} = A_{(x)}e^{-E_{(x)}RT.} \qquad (5)$$

$$\ln \text{rate} = \ln\frac{dx}{dt} = \ln A_{(x)}e^{-E_{(x)}RT.} \qquad (6)$$

Plots of $\ln\frac{dx}{dt}$(rate) for different values of x—corresponding to fraction reduced in the range 0.3—0.5 against $\frac{1}{T}$ were linear and from the slopes 'E' was evaluated. The values of activation energies thus obtained are plotted in Fig. 7 and are in the range 8.4—11.5 kcal/mole.

For the catalyst 2, it can be seen that activation energies obtained by equations 4 and 5 and the Elovich equation are in close agreement.

When a reaction proceeds heterogeneously the resulting kinetics can be of the Elovich form. The index of heterogeneity therefore could be judged by applicability of Elovich equation to a process. The results show that the catalyst prepared by impregnation method is more

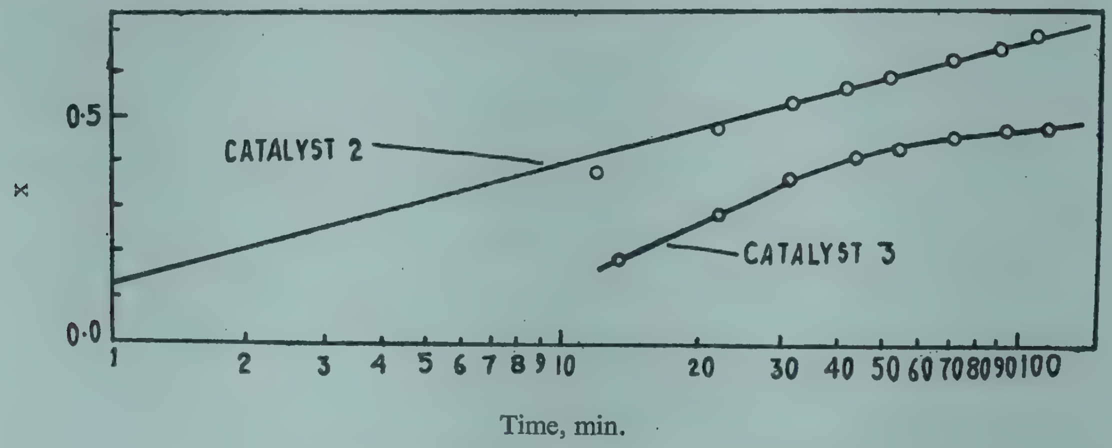

Fig. 6—Reduction of Supported Catalysts.

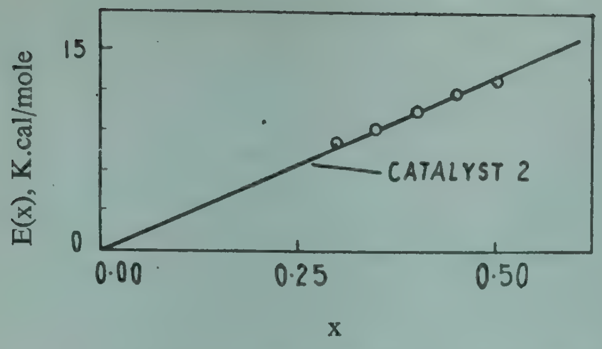

Fig. 7—Activation Energy Against Fraction Reduced.

heterogeneous. By x-ray diffraction, the phases indicated are exactly same, viz. Ni Al_2O_4 and α-Al_2O_3 as the major phases, while NiO and γ-Al_2O_3 as minor phases. It is, thus, interesting to observe that while the catalysts 2 and 3 are similar in their nickel concentration and phase composition, they differ in the degree of heterogeneity. The concentrations of the different phases in these catalysts are almost of the same order as determined by the analytical method. Levinson[17] and Bicek[18] are of the opinion that heterogeneity in the supported nickel catalyst is due to the compound formation, viz. nickel aluminate and nickel silicate, etc. between the active metal and the support which results in applicability of Elovich equation to reduction of these catalysts. The present results do not seem to confirm the contention of these authors.

Apparently, the catalyst prepared by impregnation should have better dispersion of the metal, and likely to have uniformity. But the present results indicate more uniformity in the coprecipitated catalyst. The origin of this heterogeneity in impregnated catalyst will be a subject of further investigation.

The specificity of a catalyst is related with the heterogeneity of its surface. For the development and selection of a catalyst, nature of surface heterogeneity is important. As is seen in the present investigation, the catalyst having same physical and chemical characteristics may differ in their degree of heterogeneity. Along with the latest methods, such as selective poisoning and tracer techniques, a simple study of kinetics of reduction process can give a spectrum of heterogeneity of the surface of a catalyst and can profitably be used as a method to evaluate degree of heterogeneity.

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[Original Mss. received on March 22, 1972]

UDC 541.128.34: 546.47–31+546.56–31: 546.4

Sintering properties of the copper oxide–zinc oxide type low temperature shift catalyst, calcined between 200 and 800°C, have been discussed. It has been found that significant sintering of the catalyst takes place at temperatures much lower than the Tammann points through a surface diffusion mechanism while at higher temperatures, lattice movement within the bulk of the solid was found to be responsible for extensive sintering and densification. The catalytic activity for the shift reaction was measured between 170° and 230°C. For samples calcined below 600°C, the conversion was between 90 and 98 per cent when measured at 230°C, and for the sample calcined at 800°C, the same dropped to about 50 per cent. This system showed reasonably good activity and mechanical strength up to 600°C. Curing beyond this temperature gave better mechanical strength at the expense of catalytic activity.

Studies on the Calcination of Zinc Oxide-Copper Oxide System: Effect on Physico-Chemical Parameters and Catalytic Activity

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Introduction

Curing of the powdered or pelleted catalysts is an important step in the production of catalysts. It helps in bringing out the required phase composition ultimately responsible for the catalytic activity and imparts the necessary mechanical strength to the solid. The low temperature shift conversion catalyst has a very narrow operating temperature range, viz. 170-260°C, with a heat surge capacity of about 300 to 350°C. This means that the catalyst, in its active form, can normally survive temperature spurts of this order which may result from the high exothermicity of the shift reaction itself. However, beyond the upper temperature limits this catalyst in its active form is known to be extremely sensitive to thermal changes. On the other hand, it is customary to heat-treat the oxide catalysts at higher than the operating temperatures, for better mechanical stability, which calls for a clear understanding of the sintering properties of the catalyst in the oxide form.

Sintering properties of either copper oxide or zinc oxide alone have often been reported in literature[1–4], but little attempt seems to have been made to investigate the copper oxide-zinc oxide catalyst system for its thermal stability.

The present study comprises thermogravimetric analysis of the uncured catalyst and study of the changes in the mechanical strength, surface parameters, reducibility and catalytic activity of the catalyst calcined between 200 and 800°C, the principal object being to evaluate a compromise between physico-chemical parameters and catalytic activity *vis-à-vis* curing temperatures. The catalytic activities were, however, measured within the permissible temperature limits between 170 and 230°C.

Experimental

The original catalyst sample (6 × 6 mm. tablets) used for this study was collected from a commercial production batch before curing. These tablets had been preheated at 200°C. The chemical composition on dry basis (in percentage) was copper oxide 33.78, zinc oxide 63.22 and ferric oxide 0.5 per cent. In addition to the oxides of copper and zinc, the catalyst also contained some quantities of carbonates and hydroxides formed during precipitation. 100 g. batches of the catalyst were calcined at 200, 400, 600 and 800°C, for 5 hours in a muffle furnace and the calcined samples thus obtained were then crushed and sized to 50-80 mesh (BSS) for further studies. BET surface areas, total pore volumes, average pore and particle diameters and densities were determined by the usual methods. Pore size distributions were measured with a mercury pressure porosimeter* having a maximum scanning pressure of 15,000 psi which is equivalent to a pore radius of 60 Å. The mechanical strength of the catalyst pellets was measured with a Hounsfield tensometer. X-ray phase analysis of the samples cured at 200, 400 and 800°C is given in Table 1.

TABLE 1—X-RAY ANALYSIS OF THE CALCINED CATALYSTS

Curing Temp., °C	Crystalline Phases Present		
	Major phases	Minor phases	Traces
200	CuO, ZnO	$CuCO_3$, $ZnCO_3$, $Cu(OH)_2$, $Zn(OH)_2$	α-Quartz, α-Fe_2O_3
400	CuO, ZnO	—	α-Quartz, α-Fe_2O_3
800	CuO, ZnO	Cu_2O	α-Quartz, α-Fe_2O_3

This shows the presence of carbonates and hydroxides of copper and zinc as minor phases in the original sample (200°C) along with their oxides. In the intermediate sample (400°C), the catalyst has only the oxides of copper and zinc whereas the final sample (800°C) contains cuprous oxide as a minor phase along with copper and zinc oxides.

Thermogravimetric analysis of the original sample was made on a helical quartz spring microbalance with a quartz bucket suspended from quartz fibres. The bucket carrying about 1.0 gm. of sample was directly surrounded by a furnace. Thermocouple for measuring the sample temperature was placed close to the sample bucket. The furnace was manually programmed to heat the sample at the rate of 5°C/min. Sensitivity of the balance was about 0.01 gm.

Reduction characteristics of all the catalysts were studied in the quartz spring balance using a flow of purified hydrogen. After the reduction experiments, BET surface area of the samples was measured in the same balance using low temperature nitrogen adsorption. The samples discharged from the balance were used for the measurement of pore size distribution.

For the activity measurements of water-gas shift reaction, thec atalysts were reduced under identical conditions in an all-glass reactor assembly. Activities were measured after stabilizing the catalysts for 4 hours at 230°C. Conversions were measured at 230, 210, 190 and 170°C respectively. Retracing the temperatures upwards showed no change in the original activity. A dry gas velocity of 10,000 hr^{-1} and steam-to-gas ratio of 1.0 was maintained. The feed gas contained 5 per cent carbon monoxide diluted in nitrogen. The catalytic activities were calculated as percent conversion of carbon monoxide.

Results

Table 2 shows the surface area, total pore volume and average pore and particle diameters of the calcined samples. It can be seen that the surface area records a rapid fall with increasing calcination temperature. The original sample shows a surface area of 25.6 m^2/g. On the other hand, both average pore and particle diameters show an increase in size with increasing calcination temperature. The changes in the mechanical strength and solid density of the catalysts have been shown as a function of calcination temperature (Fig. 1).

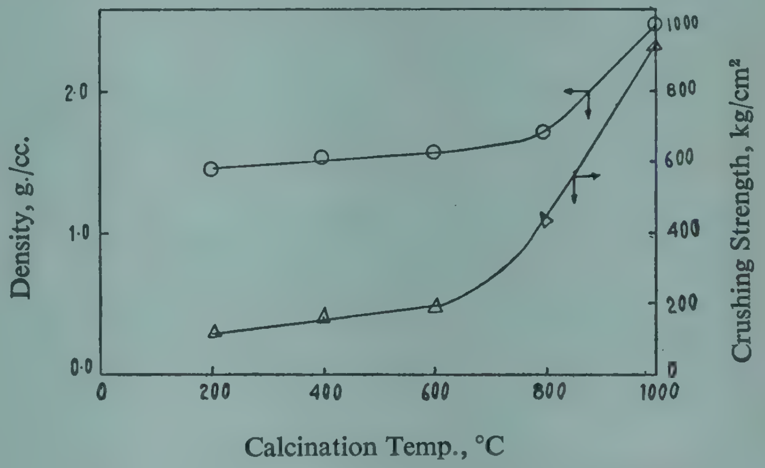

Fig. 1—Dependence of Density and Crushing Strength on Calcination Temperature.

The cumulative pore volume distribution curves shown as a function of pore radii for the samples are presented in Fig. 2. A shift in the size distribution maximum towards wider pore size as a function of temperature may be noted in these curves. While for samples calcined at 200, 400, and 600°C the pore volumes do not change very rapidly, a sharp drop in this value may be noticed for the sample heated at 800°C. This catalyst does not exhibit any porosity and consequently there is no measurable pore size distribution even in the wide pore region. The total pore volumes determined from helium and mercury displacement volumes (Table 2) are of the same order as those observed from distribution data (Fig. 2).

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* Aminco-Winslow porosimeter

TABLE 2—Surface Properties of Fresh Catalysts

Curing Temp., °C	BET Surface Area, m²/g.	True Vol., cc./g.	Apparent Volume, cc./g.	Total Pore Volume, cc./g.	Av. Pore Radius, Å	Av. Grain Radius, Å
200	25.6	0.1963	0.3883	0.1920	150	455
400	20.8	0.1686	0.3586	0.1900	183	517
600	15.7	0.1673	0.3602	0.1929	245	688
800	<1.0	0.1804	0.2116	0.0313	—	—

The TGA curve (Fig. 3) represents the weight-loss of per gramme of the original sample as a function of temperature. The step around 100°C corresponds to the removal of adsorbed moisture of the sample. Weight-loss step around 225°C indicates the decomposition of the carbonates and hydroxides of copper and zinc present in the catalyst. A weight-loss step at about 700°C is also noticeable in the curve.

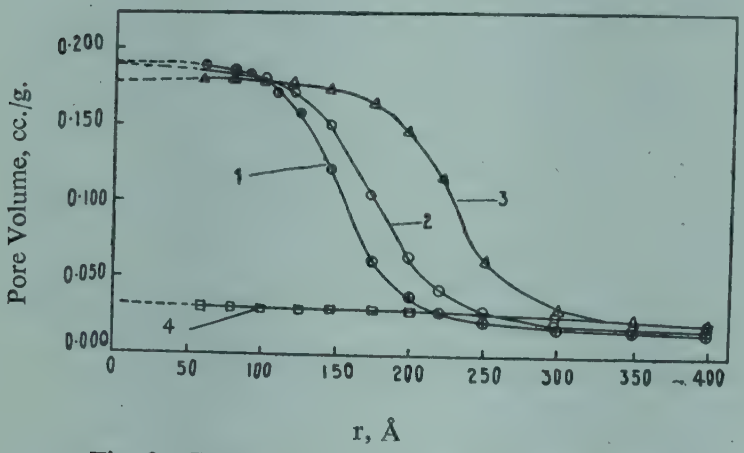

Fig. 2—Cumulative Pore Volume vs Radius Curve of the Fresh Samples.

1. Calcined at 200°C; 2. Calcined at 400°C;
3. Calcined at 600°C; 4. Calcined at 800°C.

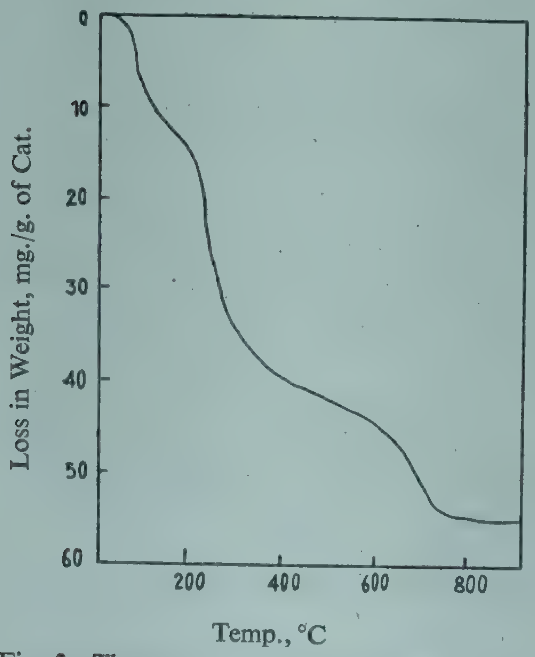

Fig. 3—Thermogram of the Uncalcined Sample.

Figs. 4 and 5 show the reducibilities of the catalysts as a function of calcination temperature. Pore size distribution curves for the reduced catalyst samples presented as cumulative pore volume vs pore radii are shown in Fig. 6. The surface areas, total pore volumes, average pore and particle radii of the reduced catalysts are given in Table 3.

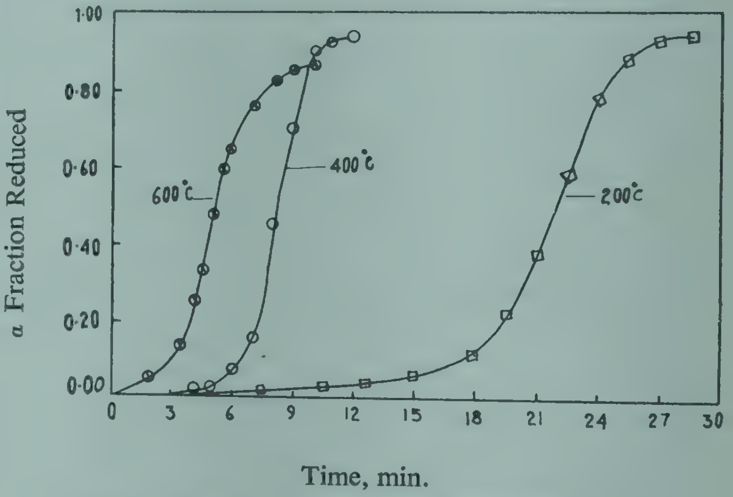

Fig. 4—Effect of Calcination Temperature on the Rate of Reduction.

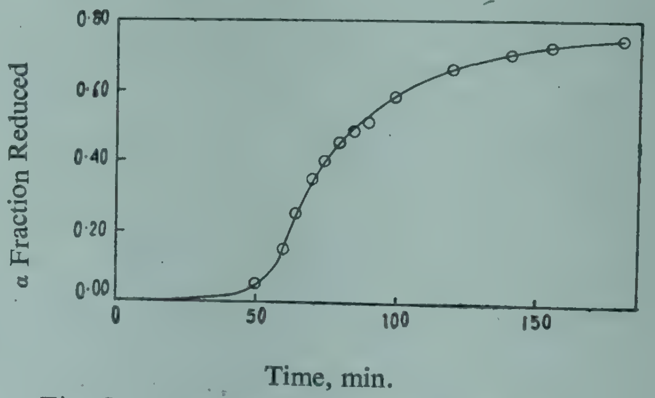

Fig. 5—Reduction of the Sample Cured at 800°C.

Discussion

Sintering and Surface Properties: Changes in the surface properties and densities of the solid substances with calcination temperatures are often used[5–6] in the study of the sintering processes. For reactions such as,

$$A_{(s)} \longrightarrow B_{(s)} + C_{(g)} \qquad (1)$$

TABLE 3—SURFACE PROPERTIES OF REDUCED CATALYSTS

Curing Temp., °C	BET Surface Area, m²/g.	True Vol., cc./g.	Apparent Volume, cc./g.	Total Pore Volume, cc./g.	Av. Pore Radius, Å	Av. Grain Radius, Å
200	22.0	0.2196	0.4483	0.2287	208	611
400	16.9	0.1383	0.3743	0.2360	266	664
600	11.9	0.1475	0.3505	0.2030	341	946
800	<1.0	0.1607	0.2134	0.0527	—	—

for hydroxides and carbonates, Dollimore and Nicholson[3] have shown that there may be one or two peaks in the surface area vs calcination temperature curves. They attribute the increase in surface areas to the stresses and strains produced in the system as a result of the difference between the specific volumes of the solid undergoing decomposition and the product formed. These forces are opposed by the sintering processes which tend to reduce the surface areas. It appears therefore that during such decompositions the surface areas must keep on increasing until the decomposition is over and the sintering processes become dominating. The second process is mainly controlled by diffusional mechanisms, such as the surface migrations beginning at Hüttig transitions[7] (0.30 Tm) and bulk or lattice diffusions occurring above Tammann temperatures.

The melting points[8] of copper and zinc oxides are 1290 and 2073°C respectively, their corresponding Tammann temperatures being 649.5 and 1036.5°C. Significant lattice mobility can, therefore, be expected for copper oxide above about 400°C and for the zinc oxide matrix above about 750°C. Gray[1] has shown that due to a high defect concentration of the surface, significant sintering can occur at temperatures far below the Tammann transition point. In the present investigation, since there is no increase in the surface area at any stage of the calcination it appears that the sintering step may be the most dominating one although the TGA curve (Fig. 3) shows that decomposition of the catalyst is not complete below 350°C. Reduction in the surface area at 400°C therefore suggests that the copper and zinc oxides have both started undergoing sintering even at such low temperatures, the rate of which according to Hüttig may be dependent on the ratio of the calcination temperature to the melting point of the oxide, expressed in the absolute scale. In fact, Dollimore and Nicholson[3] have suggested that copper oxide may experience surface diffusion at a temperature as low as 259°C. An inspection of the catalyst after treatment at 800°C clearly showed the texture to be similar to that of a soldified melt and resulted in a sharp drop in the surface area and total pore volume. The mechanical strength and the bulk density of the catalyst register a slow rise up to 600 and 800°C respectively (Fig. 1). In order to find the trend of these two parameters at higher temperatures, the original catalyst was cured up to 1000°C. The data (Fig. 1) show that the crushing strength increases sharply beyond 600°C and the density shows a similar trend beyond 800°C. Since both mechanical strength and density are bulk properties of the solid, it appears that only surface diffusion forces are responsible for the initial sintering of the solid in the regions of the curves showing slow increase in mechanical strength and density.

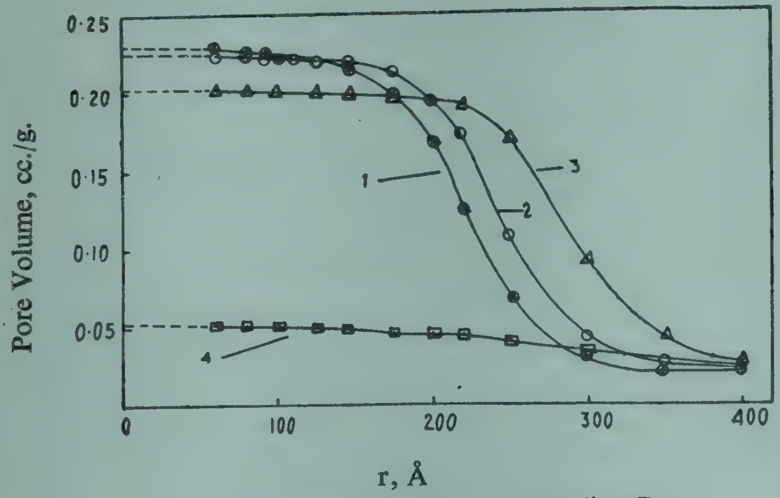

Fig. 6—Cumulative Pore Volume vs Radius Curve of the Reduced Samples.

1. Calcined at 200°C; 2. Calcined at 400°C;
3. Calcined at 600°C; 4. Calcined at 800°C.

According to Boswell and Iler[9], the sintering rates can be expressed by the following relation:

$$\log D = kT + C \tag{2}$$

where D is the number of metal atoms across one edge of an oxide lattice, T the temperature (°K) and k and C are constants. In order to express the extent of sintering in terms of a more practical parameter such as the surface area, the above equation can be modified as follows.

$$\log\left(\frac{S}{S_{max}}\right) = k\alpha + C \tag{3}$$

where S_{max} is the maximum surface area shown by the catalyst, S the surface area at any temperature T (°K), and α is the ratio of T and Tm the melting point (°K) and k and C are constants. Thus, if the logarithms of the ratio S/S_{max} are plotted as a function of α, it should result in a straight line whose slope will give the rate of sintering. Fig. 7 shows two such straight lines for the catalysts, one for copper oxide and the other for zinc oxide based on their respective melting points. It may be noted that on both the straight lines, the points for heating at 800°C, shown as dotted notations, have been obtained by extrapolation. Both these points correspond to a surface area of 13.1 m²/g. This means that if there was no appreciable lattice movement at this temperature the surface area of the catalyst calcined at 800°C would be 13.1 m²/g. However, from Table 1 it is obvious that this sample has an area of less than 1 m²/g. It can be observed therefore that equation (3) is valid in the surface diffusion region and that this relationship is of considerable importance from the catalytic point of view because it can speak unequivocally about extent of sintering of the solid over a wide temperature region, in terms of changes in the surface area. This aspect of thermal treatment also calls for a close control of curing temperature and time in order to maintain uniform textural properties in the catalysts during production.

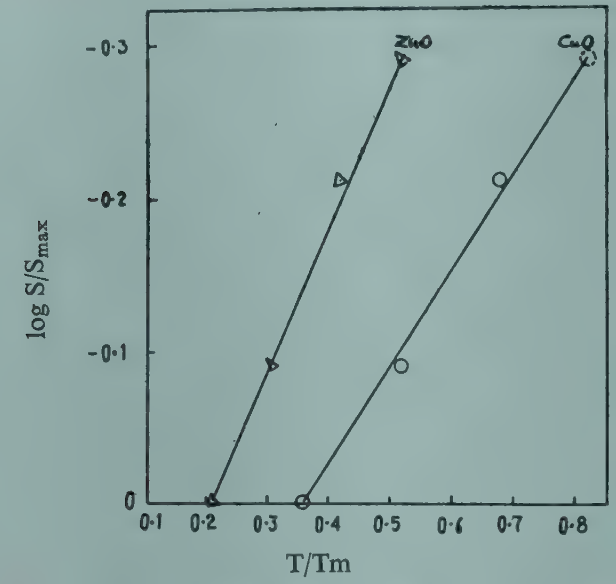

Fig. 7—Rates of Sintering of Copper and Zinc Oxides in the Catalyst.

Pore size distribution curves (Fig. 2) show that the original catalyst cured at 200°C has a total pore volume of about 0.19 cc/g and a pore size maximum at about 150 Å radius. It is a monodispersed solid which means that the entire pore volume is contributed by uniformly distributed pores of 150 Å radius. However, as the calcination temperature increases to 400 and 600°C the catalyst still remains monodispersed without the appearance of a second distribution maximum, except that the original maximum shifts towards wide pore region. At 800°C this maximum disappears and results in a total loss of porosity. Normally, one expects a bidispersed pore size distribution in these catalysts, consisting of (1) intragranular micro pore size distribution and (ii) a macropore size distribution arising from the interparticular spacings. In the present case the process of sintering proceeds with increasing temperature in such a way that before a macropore size distribution develops in the catalyst, both the components interdiffuse to form a solid 'melt' with negligible porosity. This phenomenon is significant in that neither of the components in the catalyst are likely to melt before 1280°C. Fusion characteristics for the catalyst determined under oxidizing atmospheres are given below:

Initial deformation temperature = 1000°C
Softening temperature = 1250°C
Flowing temperature = 1280°C

The observations suggest that up to 800°C no deformation of the solid occurs. However, the physical characteristics of the catalyst cured at 800°C show that the drastic reduction in porosity and surface area cannot be accounted for unless bulk diffusion forces were operative around this temperature. These forces associated with the lattice movements are known to become operative above Tammann temperatures which are much below the melting points of the solid (Tammann temperature = 0.5 Tm, where Tm is the melting point of the solid).

The total loss in weight as observed from the TGA curve (Fig. 3) is about 55 mg./g. of the original catalyst which amounts to 5.5 per cent of the sample. This loss is divided over three distinct steps. The first step at 100°C is due to the elimination of the imbibed moisture from the catalyst. The second at about 250-300°C is due to the carbonates and hydroxides of copper remaining in the sample. This conclusion is supported by the x-ray phase analysis (Table 1) which shows the absence of these compounds in the sample cured at 400°C. The characteristic rounding off of this step at 350°C shows that the decomposition of the last traces of the carbonates and hydroxides is a slow process. The weight-loss at this step constitutes about 2.5 per cent. The final step at 700°C corresponds to a loss of about 15 mg. which is 1.5 per cent of the sample. The x-ray analysis (Table 1) shows the presence of cuprous oxide in the sample cured at 800°C. The loss in weight in this region can therefore be attributed to a possible auto-reductive decomposition of some of the cupric to cuprous oxide. Such a dissociation of cupric oxide, when its vapour pressure becomes 1/5th atmosphere at high temperatures, has been suggested by Mellor[10] in the following manner:

$$4\,CuO \longrightarrow 2\,Cu_2O + O_2 \tag{4}$$

Reduction and Catalytic Activity: A good deal of useful information regarding performance and stability of the catalyst can be derived from the reduction characteristics of the solids. It can be seen from Figs. 4 and 5 that the extent of reduction and initial induction periods are different for different samples. For the original sample the induction period is about 17 min, which falls gradually for samples cured at 400 and 600°C to 5 and 2 minutes respectively. However, for the sample cured at 800°C (Fig. 5) the induction period rises to about 45 min. It is interesting to note that the rise in the induction period is also associated with drastic changes occurring in the solid at higher temperatures. Obviously, therefore, as the solid is sintered, access of the reducing gas to the interior of the bulk becomes more and more restricted causing prolonged induction periods. Another interesting feature of the reduction isotherms is the decrease in the total extent of reduction with the increase in heat treatment temperature. In the case of the original sample the total fraction reduced is about 0.95 whereas the same for the sample calcined at 800°C is only 0.80. This decrease in the total reduction may also be due to the progressive sintering of the solid. The mechanism of reduction and the significance of the induction periods for copper oxide–zinc oxide type catalyst have been discussed in detail elsewhere[11].

The catalytic activity (Fig. 8) shows that for any given catalyst, an increase in the reaction temperature gives better conversion. However, when the samples calcined at different temperatures are compared, it is seen that the activity of the samples cured up to 600°C remains more or less same, and falls abruptly for the sample, heat-treated beyond this temperature. The present results appear to be at variance with those reported by Saleta *et al*[12] for the copper oxide–zinc oxide–chromium oxide type catalysts. These authors[12] found an increase in the catalytic activity with increasing heat treatment temperature up to 500°C. They attributed this increase to the increased appearance of the spinel ($ZnCr_2O_4$) as the calcination temperature was raised.

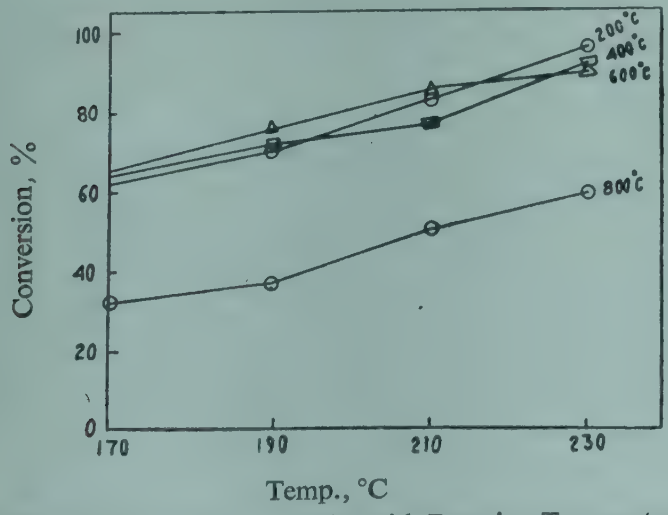

Fig. 8—Variation of Activity with Reaction Temperature.

The spinel formation during calcination in the present system is not possible due to the absence of an altervalent oxide. The progressive decrease in activity with increasing calcination temperature is therefore due to a loss of the active surface with sintering.

Conclusion

It has been shown that significant sintering of the copper oxide–zinc oxide system starts at temperatures much lower than the Tammann points through a surface diffusion mechanism, while at higher temperatures, lattice movements in the bulk of the solid are found responsible for extensive sintering. Pore size distribution data and mechanical strength of the catalyst show that the initial porosity decreases rapidly with increasing calcination temperature due to densification. Catalytic activity data points out that for samples calcined below 600°C conversion figures are fairly high ranging between 90 and 98 per cent measured at 230°C, and for the sample cured at 800°C the conversion drops sharply to about 50 per cent. It appears that calcination of the catalyst beyond 600°C gives better mechanical stability at the expense of catalytic activity.

Acknowledgement

The authors thankfully acknowledge the help of Dr. S. K. Ghosh, Dy. Superintendent (PRW), for providing the x-ray data.

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[Original Mss. received on April 24, 1973]

UDC 546.72+547.94: 541.11.036

DTA and TGA analysis show two endothermic peaks at 320 and 700°C., the first one due to dehydration of iron oxide and the second due to ferrite formation. Alkalized iron exhibits an n-type behaviour. Energy of activation (E) for electrical conductance decreased with rise in curing temperature except for the sample cured at 700°C, for which an increase was recorded.

The mechanical strength of alkalized iron pellets was found to be independent of the curing temperature up to 500°C, beyond which it is adversely affected up to 700°C and thereafter it increases with increase in curing temperature. Loss in mechanical strength in the range 500-700°C is attributed to sodium ferrite formation, which could not be confirmed by x-ray study because of its amorphous nature.

Surface area drops considerably in the range 500-600°C; at 700°C a minor increase is observed but beyond 700°C it decreased continuously up to 900°C. With increasing temperature of heat treatment finer pores are eliminated with simultaneous appearance of larger pores. Pore spectrum differs from each other except for sample cured at 600 and 700°C.

Effect of Heat Treatment on Physical Parameters of Alkalized Iron

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Introduction

Liquid hydrocarbons are desulphurized prior to steam reformation because the nickel catalyst employed for reformation is highly sensitive to sulphur-poisoning. It is achieved in two steps, viz. (1) hydrogenation of organic sulphur compounds to corresponding hydrocarbons and hydrogen sulphide over hydrogenation catalyst and (2) absorption of the hydrogen sulphide formed by suitable absorbent in the next step. Normally, the catalysts employed in industry are Comox and zinc oxide for steps 1 and 2 respectively. Since the principal constituents, cobalt and molybdenum, for Comox are not indigenously available, alkalized iron has been tried as an alternative catalyst. It removes mercaptans and disulphides quantitatively but the removal of thiophene was partial, i.e to the extent of 46 per cent in a single step operation.

Heat treatment is one of the important steps involved in catalyst preparation. It is used for achieving the requisite stability, mechanical strength and modifying the surface and structural properties of the catalyst. Its effect on different physical parameters has been investigated for various other catalysts[2–5] but alkalized iron oxide catalyst has not been studied so far. In view of above facts, the present investigation was undertaken to study in detail the effect of heat treatment on various structural and physical parameters of alkalized iron oxide. This will help in evaluating of optimum conditions for catalyst preparation and its further development.

Experimental

Catalyst was prepared by precipitating ferrous carbonate from ferrous sulphate solution by ammonium carbonate. The precipitated mass was washed till free from soluble impurities and dried at 120°C. The iron oxide so obtained was powdered to — 200 mesh size and mixed with 25 per cent alkali in the form of sodium carbonate. The resultant mass was dried at 120°C, granulated and tableted in cylindrical shape of 6 m × 6 mm size. The pellets were heat-treated in the range of 500 to 900°C in steps of 100°C. Each treatment was of 4 hours' duration with the temperature maintained within ± 5°C of the desired value. The samples (nos I, II, III, IV and V) so obtained after treatment at 500, 600, 700, 800 and 900°C, respectively were examined for surface area, pore size distribution, mechanical strength, electrical conductance and x-ray diffraction measurement. In case of DTA and TGA studies only oven-dried samples were taken.

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The mechanical strength of the samples was determined by Housefield tensometer. An average of 10 pellets tested was taken in order to have representative values of mechanical strength.

DTA thermograms were taken at a heating rate of 10°C/min. using ignited alumina as the reference material in an assembled DTA unit consisting of Gallenkamp furnace, Bausch and Lomb recorder and Ether Transitrol programmer. For TGA studies, about 50 mg. of sample was non-isothermally treated at a heating rate of 6.5°C/min. in a Stanton mass flow thermobalance with a sensitivity of 0.2 mg/div. DTA and TGA investigations were conducted under atmospheric conditions and in the range of 150 to 900°C.

Surface area measurements were carried out in a conventional all-glass volumetric adsorption unit. All the samples were outgassed at 150°C to a vacuum of 10^{-3} torr. Nitrogen was used as an adsorbate and the area of cross-section of the absorbed molecule was taken to be 16.2Å.[2]

Pore size distribution from 60 to 75000Å radius was determined by means of a 0 to 15000 psi. Aminco-Winslow mercury pressure porosimeter. The pore radii were calculated from the relationship $2r = \frac{175}{p}$ where r is the radius in microns and P is the pressure in psi. Small pressure increments dP required for forcing mercury in the volume dV of the pores of radii between r and r + dr, were determined from the experimental data for the total range of pores between 0 to 15000 psi. A plot of $\frac{dV}{dr}$ vs r gives the pore spectrum for the sample under study.

Electrical resistance measurements were conducted in air as well as under vacuum. Catalyst pellets, heat-treated at different temperatures, were regranulated and tableted into 10 × 10 mm. size to fit in the sample-holder. Pressure employed for tableting was 5000 psi. Pellets were held tightly between two platinum electrodes provided with Pt/Pt-Rh thermocouple. Temperature of the samples under study was measured by Philips GM-6001 DC Microvoltmeter and resistance by GM-6020 Volt-ohmmeter. Evacuation was carried out at 400°C to a pressure of 10^{-3} torr till a constant value for electrical resistance was recorded. This was done with a view to remove completely the adsorbed gases and moisture from the surface which may affect the electrical properties of the sample. Later the temperature was gradually lowered to 300°C under vacuum and electrical resistance measurements were made in the range 300 to 400°C in steps of 30°. The energy of activation (E) for electrical conductance has been calculated by employing the standard Arrhenius equation $R = Ro\ e^{-E/kT}$, where where R is the resistance at temperature T, Ro is resistance at temperature O°K and k = Boltzmann constant. Similar studies have been conducted in presence of air also. Purified air, free from moisture and carbon dioxide, was used for the purpose.

The x-ray diffraction studies were conducted with Philips PW-1010 model diffractometer using FeKα radiation, employing 30 KV with a current flow of 10mA.

Results and Discussion

DTA thermograms for pure and alkalized iron oxide exhibit two endothermic peaks at 135° and 320° (Fig. 1). The former is due to loss of moisture whereas the latter corresponds to the following reaction.[6]

$$2\text{-}FeOOH = Fe_2O_3 + H_2O \qquad \ldots.(1)$$

The behaviour of alkalized iron oxide differs from that of the pure one after 400°C. The pure oxide does not undergo any further change in its phase composition up to 900°C. However, in the case of alkalized iron another endothermic peak appears at 700°C (Fig. 1), which could be due to ferrite formation according to the following reaction.

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2 \qquad \ldots.(2)$$

Sodium ferrite formation has been observed earlier too, upon heating a mixture of ferric oxide with an

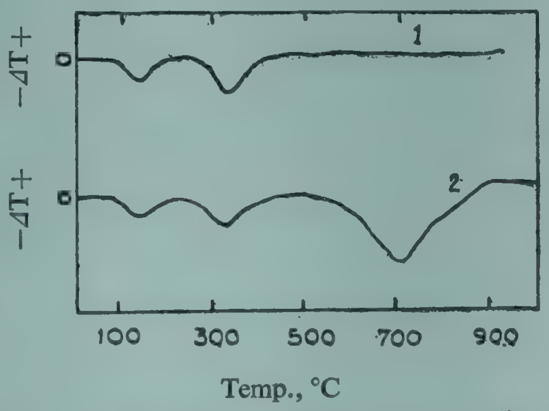


Fig. 1—DTA Thermogram of Pure (Curve 1) and Alkalized Iron Oxide (Curve 2).

alkali[7]. However, the formation of a new phase around 700°C cannot be taken as confirmed by DTA thermogram alone.

TGA thermogram provides an additional evidence in favour of the ferrite formation. A plot of $\frac{dw}{dt}$ against temperature exhibits two peaks, viz. at 264 and 660°C respectively (Fig. 2), the former corresponding to loss of moisture according to reaction 1 and the latter due to ferrite formation. Weight-loss observed at 660°C agrees well with the calculated value expected from ferrite formation. Calculated loss in weight was 38.2 mg, whereas actual estimated loss was 35.1 mg. This in turn confirmed the interaction between iron oxide and sodium carbonate leading to ferrite formation.

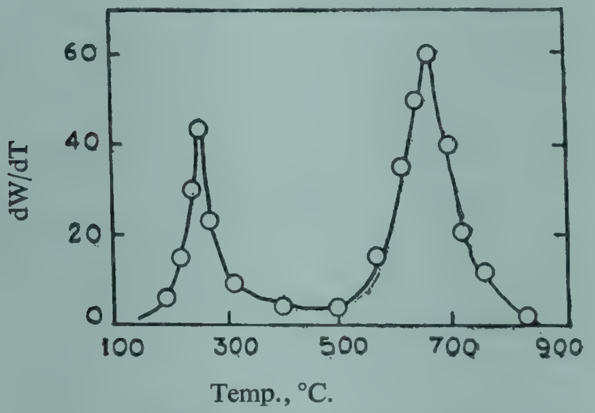


Fig. 2—DTA Thermogram of Alkalized Iron.

Electrical conductance studies also provide additional evidence about the formation of ferrite at 700°C. All the samples exhibited higher electrical resistance in air than in vacuum indicating an n-type behaviour of the catalyst. This is in agreement with earlier workers[8]. Resistances in all the cases decreased with increasing temperature and a plot of log R vs $\frac{1}{T}$ is linear (Fig. 3). Energy of activation E for electrical conduction decreased with increase in curing temperature for all the samples, except in sample III. In this case, the conduction is increased (Fig. 4) and the rise in E indicates appearance of a new phase, which is responsible for this anomalous behaviour.

Sodium ferrite so formed could not be detected by x-ray diffraction studies indicating its amorphous nature. Using of x-ray analysis, presence of only α-Fe_2O_3 and traces of unreacted sodium carbonate hydrate could be detected. Free Na_2O was found to be totally absent.

It is clear from all the studies mentioned above that a new phase, viz. sodium ferrite, starts appearing in the system at 500°C. In the temperature zone 500 to 600°C, the rate and extent of formation are very small. Beyond 600°C, it is fairly high and transformation is complete at 700°C and the new species formed, i.e. sodium ferrite, is amorphous in nature.

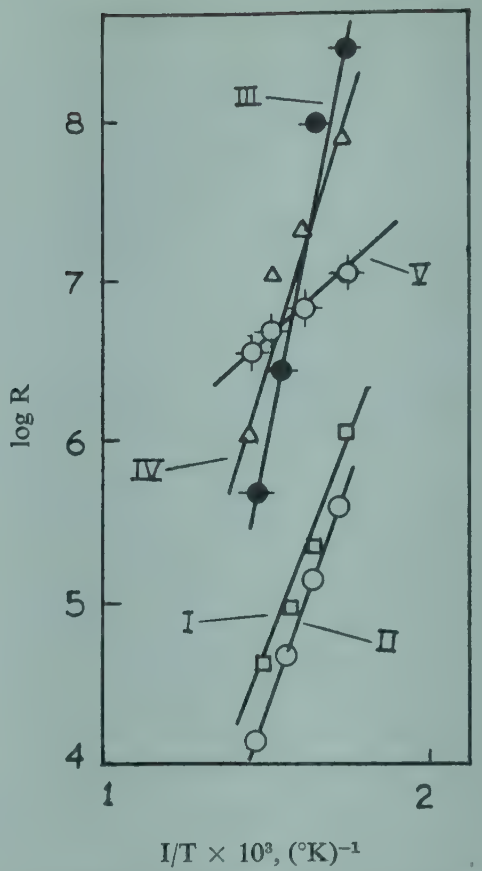


Fig. 3—Variation of Resistance with Temperature in Vacuum in Different Samples (I, II, III, IV & V).

The formation of ferrite is reflected in various other properties of the catalyst. Heat treatment is one of the standard techniques employed for improving the mechanical strength of catalysts and normally it improves with rise in curing temperature[9]. This is due to increase in crystallite size through sintering. However, in the present case, mechanical strength remained unchanged by heat treatment up to 500°C. Thereafter, it decreased

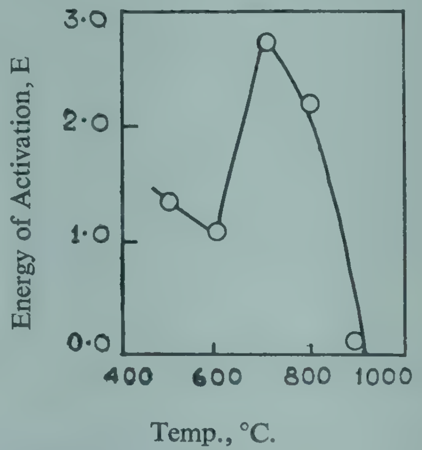
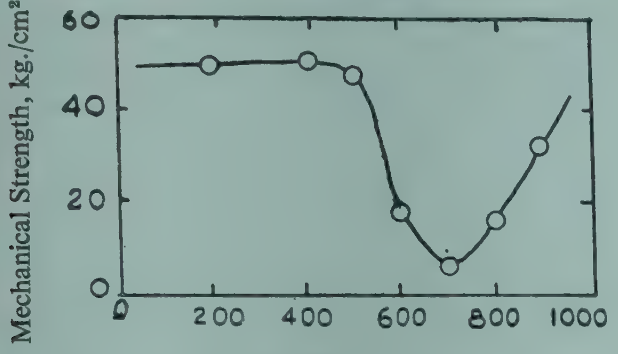


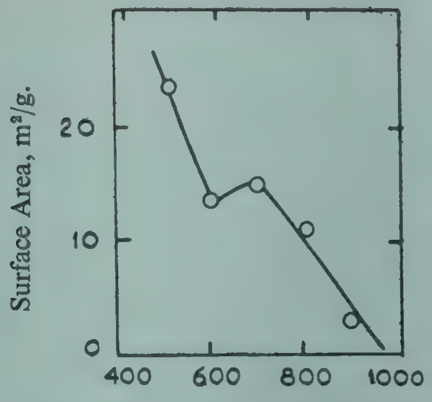
Fig. 4—Effect of Curing Temperature on Energy of Activation for Electrical Conductance.

with rise in the curing temperature up to 700°C, beyond which it again improved (Fig. 5). Fall in mechanical strength in the range of 500 to 700°C may be due to lattice distortion caused by the interaction of alkali with iron oxide. Deterioration is more rapid in the range 600°700°C, where probably the reaction approaches fast and transformation to ferrite is complete.



Curing Temp., °C.
Fig. 5—Effect of Heat Treatment on Mechanical Strength.

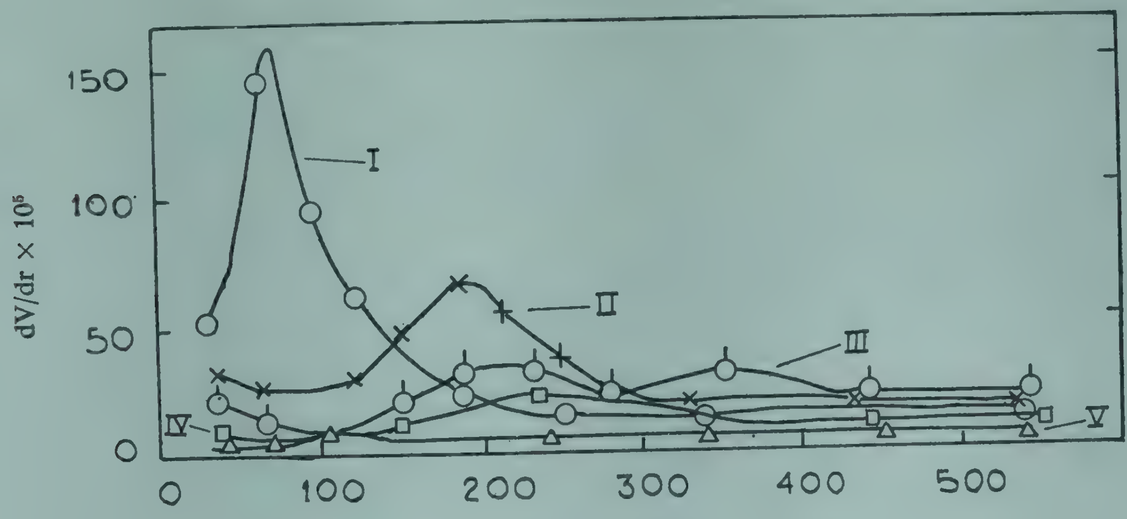
Specific surface area drops sharply with increase in curing temperature from 500 to 600°C. A minor increase is observed at 700°C and thereafter the surface area decreases progressively with rise in temperature (Fig. 6). In case of pure iron oxide, Sen *et al*[2] observed a continuous fall in surface area up to 800°C. Unusual behaviour observed in the present case between 600 to 700°C appears to have a link with the formation of sodium ferrite, which is amorphous in nature. The other factor, which may contribute towards arresting the fall in surface area which normally should occur under the influence of the sintering force, is evolution of CO_2 formed during interaction. These two processes actually balance the loss in surface area caused due to sintering. However, beyond 700°C, sintering again predominates (Fig. 6).



Curing Temp., °C.
Fig. 6—Effect of Heat Treatment on Surface Area.

Pore size distribution has been presented as $\frac{dv}{dr}$ vs $\bar{r}$ (Fig. 7). It may be observed that there is a regularity in the distribution pattern of the curve, as the curing temperature is increased from 500 to 900°C. At the lowest temperature of curing, the curve has a sharp peak at 60-80Å and beyond this range the pore volume is covered by pores having diameter distributed over a wide range. As the temperature of curing is increased the curves are flattened and at the same time the peak is shifted towards the right hand side. This trend continues up to maximum temperature of curing. Sample III appears to have different pattern of distribution than others. It has two broad peaks at 150-250Å and between 300-400Å. At higher temperature of curing sharp distribution is practically absent and $\frac{dv}{dr}$ remains almost unchanged with increasing $\bar{r}$.

Absence of uniform pores in samples cured at higher



Pore Radius, rÅ
Fig. 7—Effect of Heat Treatment on Pore Size Distribution in Samples I, II, III, IV, V.

temperature may have undesirable influence on selectivity and may be taken as guidance in formulation of catalyst.

Acknowledgement

The authors wish to thank Dr. S. K. Ghosh for furnishing the x-ray analytical data.

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[Original Mss. received on March 18, 1973]

UDC 541.128.04

The initial activity of most catalysts is fairly high but decreases with use on stream and temperature of operation. The activity falls rapidly at first but then declines much more slowly with time. Experiments have been carried out with high temperature shift catalyst in the temperature range of 350-500°C to determine the decrease in activity of P & D catalyst in a small pilot plant working at a pressure of 30 kg. cm^2. The gaseous mixture used for the reaction has been taken from a commercial shift converter of F.C.I., Trombay. Rate constants have been calculated for different periods, the experiment having completed 3000 hr of operation is still being continued. The study has been utilised in the evaluation of actual design activity for sizing industrial reactor taking the average life of a shift catalyst to be three years. The experimental data have been suitably processed for computer programming to be utilised in designing shift converters of future fertilizer plants.

Shift Catalysts—Their Activity and Life*

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Introduction

Synthesis gas for the manufacture of ammonia is normally produced from feedstocks containing carbon, such as coal, lignite, naphtha, fuel oil and gases, e.g. natural gas, coke oven gas, etc. Oxides of carbon are almost always present in the reaction products which however must be removed before they can be used for ammonia synthesis as they deactivate the synthesis catalyst. The removal of carbon monoxide is carried out in stages, through the shift reaction,

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*Paper presented at the Silver Jubilee Session of the Indian Institute of Chemical Engineers held at I.I.T., Delhi during Dec. 2-8, 1972.

$$CO + H_2O = CO_2 + H_2 \ldots. \quad 9.84 \text{ K.cal},$$

in the presence of chromia promoted iron oxide catalyst working in the range 350-500°C and pressure atmospheric to as high as 30 kg/cm². The conventional shift reaction not only removes the impurity but also increases the hydrogen efficiency of the system. The remaining carbon monoxide is removed either by absorption with suitable solvents or by low-temperature shift in the presence of a copper-catalyst working in the temperature range of 200-250°C thus bringing the carbon monoxide to as low as 0.3-0.4 per cent. The use of copper-based low temperature shift catalyst however requires very pure gas streams and has been used only in plants using naphtha steam reformation process. The shift reaction in commercial plants is carried out in adiabatic converters containing catalysts in single or multiple beds depending on the initial concentration of carbon monoxide. The reaction being exothermic, high conversions are favoured by low-temperatures but the rate of reaction increases as the temperature is raised. The shift conversion process was first developed by Bosch and Wild[1] in 1912 and used for commercial production by BASF in Oppau a few years later. The shift catalysts, both high and low temperature, being so vital for the manufacture of ammonia, FCI's P & D Division have developed their know-how and are producing them commercially.

A literature survey on this important unit process of chemical reaction engineering reveals that various workers[1-4] have studied different aspects of the kinetics of this reaction. Laupichler,[2] Atwood[3] and Mars[4] have postulated a first order reaction to arrive at a simplified rate equation. Moe[7] and others have chosen a second order reaction mechanism to formulate a design equation. The present authors[5,6] also studied the kinetics of both chromia-promoted iron oxide and copper-zinc low temperature shift catalysts at working pressure up to 30 kg./cm², assuming a first order reaction and arrived at a simple design rate equation which has been used for sizing of industrial reactors. In the previous experiments they have studied the variation of temperature and pressure in an isothermal reactor and deduced a kinetic expression. According to their experience from laboratory experiments as also in commercial shift converters, the activity of the catalyst is initially very high up to 100-150 hours but gradually decreases with time. The rate of fall of activity is quite fast during 150 to 400 hours, comparatively less fast between 400 and 700 hours, after which the decrease is practically steady up to 1000 hours. After 1000 hours, the activity of the catalyst becomes more or less constant. The experimental observation as also the rate coefficients calculated show the decrease in catalyst activity with age and operating temperature.

The present authors' experimental observation and evaluation are almost in agreement to those of Mars[4], Hoogschagen[9] and Moe[7]. Hoogschagen and Zwietering[9] have tried to establish a quantitative relationship between the decrease in surface area of a catalyst with its age at different operating temperatures. The temperature chosen is however somewhat above the normal operating temperature of a shift catalyst. Their observations have been correlated by the following equation:

$$\frac{1}{A^n} - \frac{1}{A^n_o} = Kt \exp(-E/RT) \ldots.$$

where A_o = original surface area
t = time
n = experimentally determined constant.

The surface area of a shift catalyst predicted by the above equation is given in Table 1. The decrease in surface area for working temperatures between 350 and 450°C is negligible whereas an abrupt change is predominant above 450°C. These observations, however, agree well with those of Mars[4], who found that Hoogschagen's relationship holds good for working temperature above 500°C, whereas at lower temperatures the actual loss of activity is much more than the decrease in surface area. According to Moe's[7] observation, neither the surface area nor the decrease in activity can be quantitatively correlated by any relationship and as such he suggests lengthy experiments. Experience from industrial reactors which have been followed in the present work is the best guide for the selection of the rate constant which should be used for design purposes.

A regular charge of commercial catalyst is expected to give the designed output throughout the useful life period which in most cases is 2-3 years. The catalyst manufacturer very often prefers to supply an extra volume over what is calculated from the kinetic data and the

TABLE 1—SURFACE AREA OF A SHIFT CATALYST (PREDICTED)

Temp., °C	A (after 12 months)
350°C	31.80
360°C	31.65
390	30.90
400	30.35
420	27.45
450	21.85
500	14.80
550	10.39

A = Surface area.

designer also favours a safety margin, but even after all these precautions failure of the catalyst to supply the specified design output throughout in operational units may not be completely absent. The decrease in the activity of the catalyst may be attributed to the structural changes inside the catalyst pellets due to thermal sintering, change in surface area, decrease in active sites where the actual reaction occurs and the poisoning effect of certain gases, such as hydrogen sulphide. The present study was undertaken with the object of determining the activity at different time periods during the long time life tests carried out to measure quantitatively the decrease in activity of the FCI catalyst and hence to evaluate its industrial life with time.

Experimental

The whole set of experiment has been carried out in the ammonia plant of FCI's Trombay Unit. The wet gas used for reaction is obtained from a side stream of the gas passing on to the shift converter having the following composition (per cent): carbon dioxide 4.6, hydrogen 52, carbon monoxide 40.4, methane 0.4 and nitrogen rest; S/G ratio 0.9-1.3. The experiment was carried out in the pilot plant used earlier having an isothermal reactor using 100 cc of high temperature shift catalyst (K.S. 308) of size 3 × 6 mm, pressure remaining almost constant (28 kg./cm^2.g.); space velocity in the range of 9,500-10,000 hr^{-1}. The rate of fall of activity with time depends on the operating temperature and hence studies have been made keeping the catalyst for a sufficiently long duration at each successively increased temperature in the operating range. The catalyst after reduction was heated to 360°C maintaining a gaseous space velocity 10,000 hr^{-1}. The inlet and outlet gas samples were analysed at regular intervals. The experiment at 360°C was continued up to 1,096 hours after which the catalyst bed temperature was raised to 390°C, stabilized, maintained for 778 hours during which the fall in activity was recorded. Six different sets of experiments were carried out at 360, 390, 420, 450, 480, 510°C with the same catalyst, the total test period being 3,764 hours, i.e. approx. 160 days. There has been a number of shut-downs and start-ups during this period due to operational/maintenance problems in the plant as also due to power failure. The catalyst after discharge was found fouled by a large quantity of very fine carbon particles carried by the gas stream. The results are given in Table 2, along with the calculated rate coefficients corrected for pressure in the same manner as in our previous work.[6] The pressure corrected rate coefficients have been correlated against time in a semilog graph at each of the respective temperature (Figs. 1 to 5).

Results and Discussion

The nature of fall of catalyst activity with time has been studied at different temperatures (Figs. 1-5), where the rate of reaction corrected for pressure has been plotted against time for different temperatures. The sintering factor, which accounts for the decrease in the activity of the catalyst, is a function of temperature and hence the experiment was started with 360°C as catalyst bed temperature taking particular care that the temperature does not rise above 360°C. The catalyst was kept at this temperature for 44 days and the results plotted (Fig. 1). It has been observed that the catalyst is highly active in the beginning but rapidly loses its activity due to thermal sintering which decreases its surface area within 15-20 days. Between 20-40 days the rate of decrease in

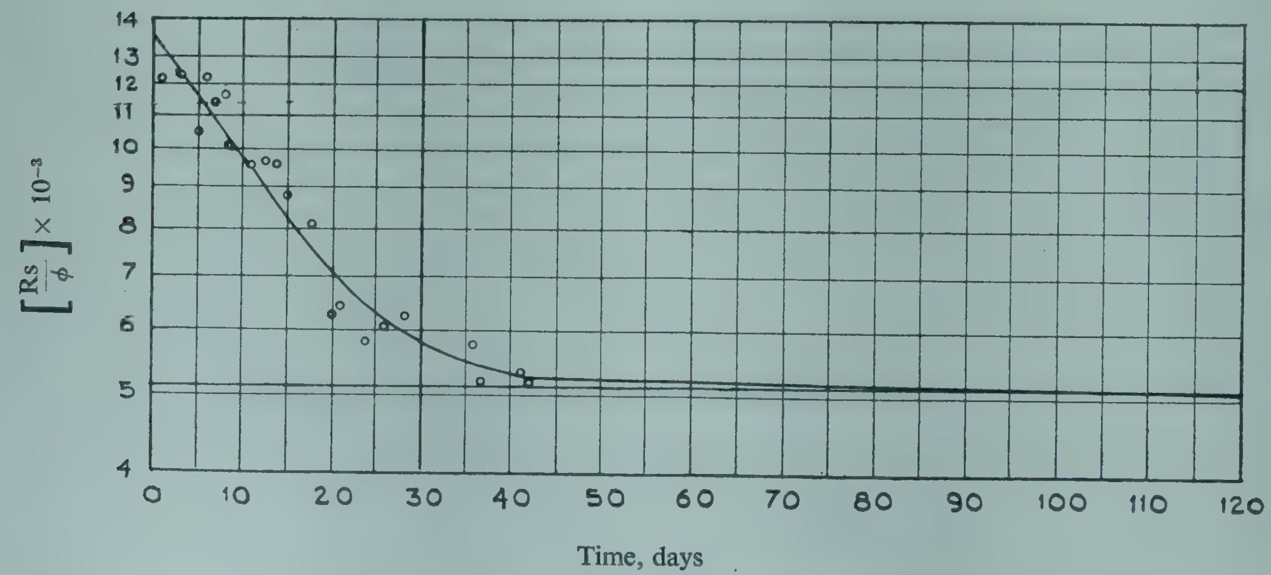

Fig. 1—Fall of Catalyst Activity with Time at 360°C.

TABLE 2

Experimental Observation									Calculated		
Total Hours of Run	No. of Days of Run	Pressure in Atmosphere, Abs.	Exit S.V.	Steam Gas	Temperature, °C Inlet	Temperature, °C Outlet	Exit Gas Composition, % CO_2	Exit Gas Composition, % CO	$R_s \times 10^4$	$R_s/P\left(.5 \frac{-P}{250}\right) \times 10^3$	$\frac{1}{T^0} \times \frac{10^{-3}}{K}$
1	2	3	4	5	6	7	8	9	10	11	12
24	1.0	27.5	9900	1.02	360	360	30.3	3.4	4.495	12.3	1.58
74	3.08	26.5	9900	0.96	360	360	29.8	3.6	4.495	12.35	1.58
124	5.16	25.5	9900	0.88	360	360	28.6	4.2	3.820	10.5	1.58
145	6.05	26.5	9900	1.02	360	360	30.0	3.4	4.495	12.35	1.58
172	7.16	26.2	9900	0.99	360	360	29.6	3.8	4.150	11.40	1.58
197	8.20	26.5	9900	0.96	370	370	28.8	4.0	4.250	11.695	1.559
215	8.95	26.5	9900	0.96	360	360	28.4	4.4	3.685	10.11	1.58
265	11.05	27.0	9900	1.05	360	360	28.4	4.6	3.480	9.55	1.58
311	12.95	25.5	9900	0.99	360	360	28.8	4.6	3.52	9.65	1.58
336	14.00	27.0	9900	0.99	350	355	28.0	4.8	3.48	9.55	1.58
362	15.10	27.5	9900	0.96	360	360	28.6	5.2	3.199	8.75	1.58
431	18.0	27.0	9900	0.96	360	360	28.0	5.8	2.920	8.02	1.58
480	20.0	26.5	9900	0.91	350	355	26.8	7.6	2.278	6.25	1.60
506	21.1	25.0	9900	1.02	360	360	26.8	7.8	2.310	6.40	1.58
537	22.4	27.4	9900	0.99	360	360	26.4	8.0	2.285	6.26	1.58
573	23.85	27.0	9900	0.91	360	360	26.0	8.4	2.11	5.80	1.58
624	26.0	27.5	9900	0.90	360	360	26.2	8.2	2.205	6.05	1.58
678	28.2	22.0	10200	0.96	360	360	25.8	8.2	2.230	6.25	1.58
[Unit was shut down after 694 hours due to shut-down of Ammonia Plant]											
860	35.8	26.8	9900	0.87	360	360	26.6	8.4	2.10	5.76	1.58
884	36.8	24.2	9900	0.87	360	360	25.4	9.8	1.88	5.2	1.58
987	41.1	27.8	9900	0.99	360	360	25.0	9.8	1.93	5.3	1.58
[Unit was shut down due to shut-down of Ammonia Plant]											
1059	44.0	28.0	9900	0.99	360	360	24.8	10.0	1.893	5.2	1.58
[Temperature raised to 390°C]											
1089	45.4	28.2	9900	1.05	390	390	28.0	4.4	3.48	9.55	1.51
1137	47.4	28.0	9900	0.88	390	390	28.0	5.6	3.51	9.625	1.51
1285	53.5	25.5	9900	0.90	390	390	28.0	5.6	3.505	9.65	1.51
1324	55.1	24.0	9900	0.98	390	390	27.8	6.0	3.179	8.82	1.51
[Shut-down due to heavy CO leakage]											
1372	57.2	28.0	9900	1.07	390	390	28.0	5.6	3.905	9.095	1.51
1415	59.0	28.0	9900	0.96	390	390	28.0	5.4	3.485	9.55	1.51
1439	60.0	28.0	9900	0.99	390	390	28.2	5.4	3.62	9.93	1.51
1461	61.0	28.0	9900	1.07	390	390	28.2	5.6	3.30	9.05	1.51
1510	62.99	28.5	9900	1.26	390	390	27.8	5.8	3.28	8.999	1.51
1522	63.5	28.5	9900	1.24	390	390	27.6	6.0	3.20	8.755	1.51
1611	67.1	28.5	9900	1.02	390	390	27.8	6.2	3.1	8.50	1.51
1851	71.1	27.5	9900	1.10	390	390	26.8	7.0	2.84	7.65	1.51
1955	81.50	27.5	9900	1.10	390	390	26.8	7.0	2.84	7.65	1.51

TABLE 2 (*Contd*)

Experimental Observation									Calculated		
Total Hours of Run	No. of Days of Run	Pressure in Atmosphere, Abs.	Exit S.V.	Steam Gas	Temperature, °C Inlet	Temperature, °C Outlet	Exit Gas Composition, % CO_2	Exit Gas Composition, % CO	$R_s \times 10^4$	$R_s/P\left(.5 \frac{-P}{250}\right) \times 10^3$	$\frac{1}{T^0} \times \frac{10^{-3}}{K}$
1	2	3	4	5	6	7	8	9	10	11	12
[Temperature raised to 420°C]											
2057	85.5	28.0	9900	0.95	420	420	28.2	5.8	3.98	10.92	1.44
2105	87.9	28.0	9900	0.86	420	420	28.0	5.8	4.445	12.2	1.44
2153	89.5	28.0	9900	0.91	420	420	27.8	6.0	3.905	10.7	1.44
2177	90.5	26.5	9900	0.84	420	420	27.8	6.0	3.9	10.5	1.44
2227	92.9	27.5	9900	0.84	420	420	27.6	6.2	4.19	11.49	1.44
2271	94.5	27.5	9900	0.91	420	420	27.4	6.4	3.7	10.0	1.44
2321	96.9	27.5	9900	0.84	420	420	27.4	6.6	3.74	10.26	1.44
2380	99.1	27.5	9900	0.75	420	420	26.6	7.2	3.95	10.81	1.44
2393	99.6	27.5	9900	0.96	420	420	26.4	7.4	2.99	8.18	1.44
2418	100.8	27.5	9900	1.02	420	420	26.0	7.8	2.73	7.5	1.44
2513	104.9	27.5	9900	1.87	420	420	25.8	8.2	2.76	7.55	1.44
[Shut-down due to annual shut-down after 2521 hours]											
3014	125.8	27.5	9900	1.02	420	420	26.6	7.8	2.82	7.75	1.44
[Unit was shut-down due to power failure] [Temperature raised to 450°C]											
3043	—	24.5	9900	1.21	450	450	28.0	6.6	3.95	10.95	
3089	128.9	24.5	9900	1.08	450	450	28.4	6.4	4.15	11.41	1.385
3209	—	26.0	9900	0.91	450	450	28.4	6.6	4.39	12.05	1.385
3221	134.1	26.0	9900	0.91	450	450	28.0	6.8	4.33	11.9	1.385
3231	134.9	26.0	9900	0.99	450	450	27.4	7.4	3.6	9.9	1.385
3255	135.7	26.0	9900	0.96	450	450	27.2	7.6	3.37	9.26	1.385
3284	137.0	25.5	9900	0.93	450	450	27.0	7.8	3.27	9.00	1.385
3391	141.1	24.0	9900	0.96	450	450	27.0	8.0	3.15	8.72	1.385
[Temperature raised to 480°C]											
3401	142.0	24.0	9900	0.93	480	480	26.4	8.6	3.035	8.4	1.33
3438	143.0	25.0	9900	0.93	480	480	26.2	8.8	3.035	8.4	1.33
3525	147.0	27.0	9900	1.02	380	480	26.4	9.2	2.92	8.0	1.33
3616	150.5	26.5	9900	1.05	480	480	26.6	9.0	3.1	8.54	1.33
[Temperature raised to 510°C]											
3629	131.0	26.5	9900	1.07	510	510	28.0	8.6	3.84	10.15	1.277
3674	153.0	26.0	9900	1.07	510	510	26.6	9.0	3.62	9.94	1.277

Rs = Reaction rate Coefficients.

$\frac{Rs}{P\ (.5\text{-}P/250)}$ = Reaction rate Coefficient after pressure correction.

activity is much slow and after 40 days it reaches a more or less steady value which is indicated by the constant exit gas composition from the reactor. The period after 40 days may be called a slow-steady fall period.

The temperature of the catalyst bed was raised to 390°C after 44 days and was maintained at this temperature till the beginning of the next slow-steady fall period which was found after 77th day. To be certain about the steady fall period, the experiment was continued up to the 82nd day and confirmed by the constant gas composition from the reactor. Another important observation worth mentioning is that on raising the temperature from 360 to 390°C a sudden rise in activity, nearly 1.86 times, was observed due to a rise of catalyst temperature by 30°C. The fall of catalyst activity (from Fig. 2) was quite slow during the first 15 to 20 days at 390°C also but after 20 days this was found to be accelerated and the steady fall period was observed after 34 days of operation.

Similar observations were noted when the catalyst bed temperature was raised to 420°C (Fig. 3) and 450°C (Fig. 4) subsequently. The catalyst activity was found to be increased nearly 1.50 times by the sudden rise of

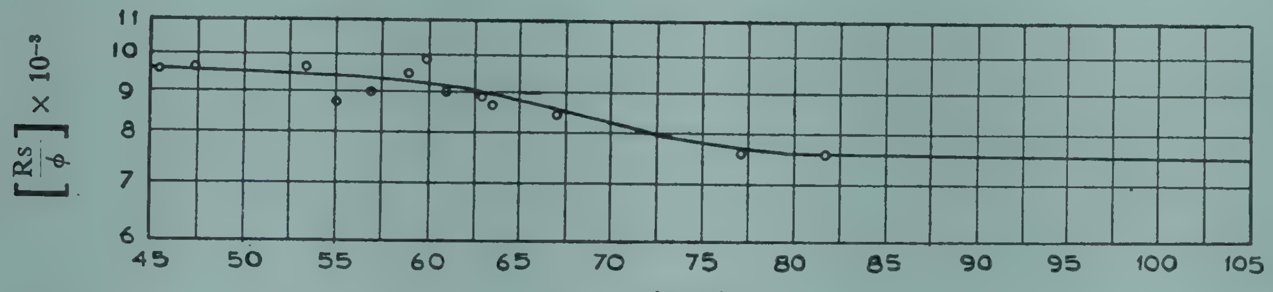

Fig. 2—Fall of Catalyst Activity with Time at 390°C.

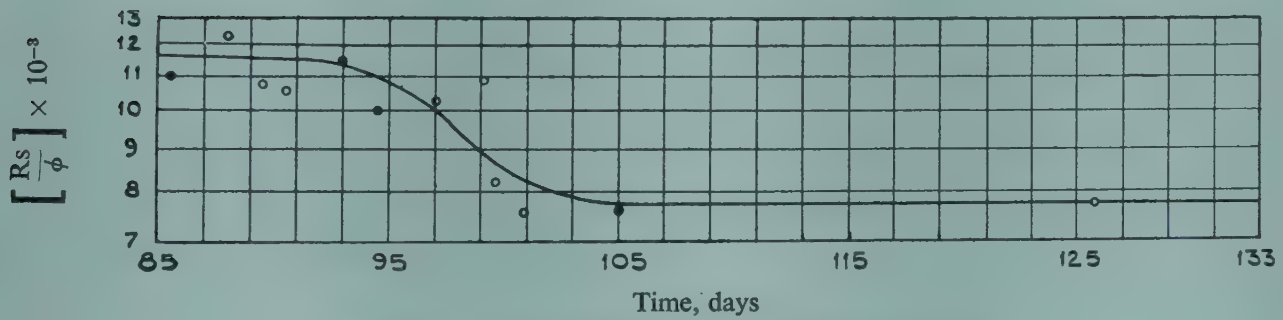

Fig. 3—Fall of Catalyst Activity with Time at 420°C.

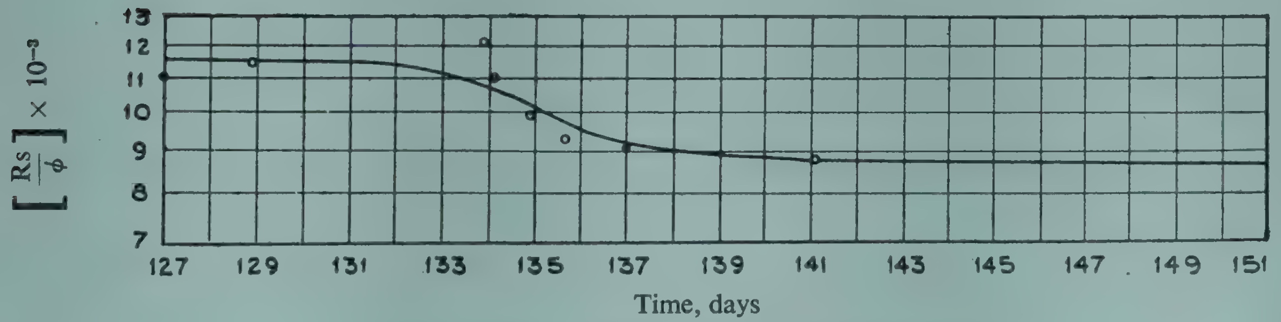

Fig. 4—Fall of Catalyst Activity with Time at 450°C.

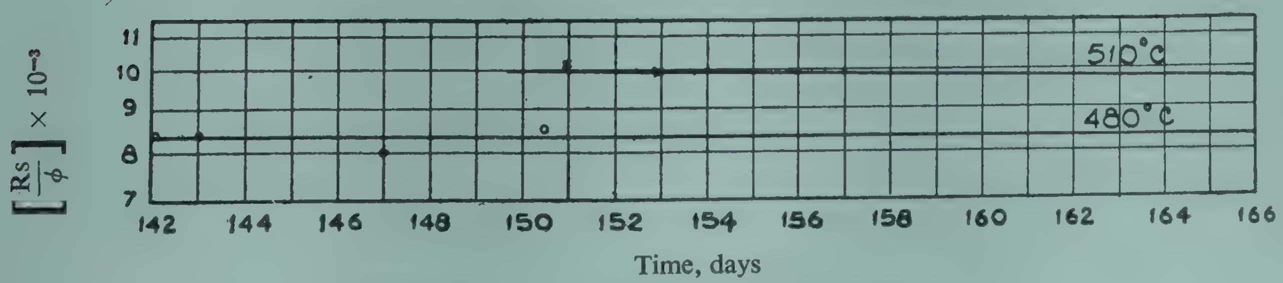

Fig. 5—Fall of Catalyst Activity with Time at 480 and 510°C.

temperature (i.e. by 30°C) to these temperatures in the beginning (i.e. on the 85th and 127th days).

The catalyst temperature was raised from 450 to 480°C (on the 142nd day) but surprisingly no rise in activity was observed in this case. The catalyst was kept at 480°C up to 150.5th day and finally raised to 510°C when again there was some rise in activity (Fig. 5). The lower activity of the catalyst (compared to its expected values) after 142nd day in the beginning of 480°C may be explained by the fouling of the catalyst by carbon deposited over its active surface, which was found in the discarded catalyst. Feed gas is suspected to be the carrier of carbon.

The equations for slow and steady fall period at different catalyst temperature were derived from Figs. 1 to 5 (Table 3). The catalyst activity was approximately extrapolated to 1000 days by these equations. The sudden rise in catalyst activity with rise of temperature (described earlier) was carefully noted and tabulated (Table 4). This data was used to evaluate the apparent activation energy (E = 13.88 K. cal/g.mol) (Fig. 6). Initial activity (i.e. on the 1st day) was evaluated at different temperature by knowing the same for 360°C and the relative activities at different temperature (Table 4).

The sintering factor on 1,000 days at 400°C was found to be 0.22 previously[6], which is in close agreement with the present value obtained (Table 3).

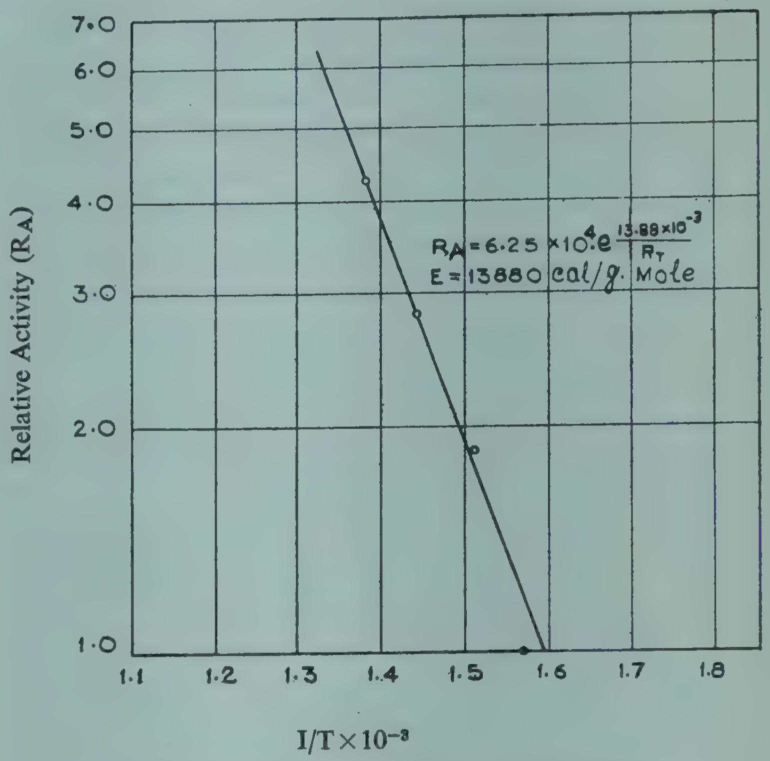

Fig. 6—Variation of Relative Activity with Temperature.

TABLE 3—'SINTERING FACTOR' OF CATALYST ON 1000 DAY AT DIFFERENT TEMPERATURE

Fig.	Catalyst Temp. °C	Equation for steady fall Period	R_s/ϕ on1000 day (by approximate extrapolation)	R_s/ϕ on 1st day	Sintering Factor on 1000 day	Remarks
1.	360°	$\frac{R_s}{\phi} = (5.36 \times 10^3) \times 10^{-(2{\cdot}0 \times 10^{-4})t}$	3.39×10^3	12.3×10^3	0.27600	
2.	390°	$\frac{R_s}{\phi} = (7.80 \times 10^3) \times 10^{-(1{\cdot}5 \times 10^{-4})t}$	5.515×10^3	22.90×10^3	0.2410	
3.	420°	$\frac{R_s}{\phi} = (7.85 \times 10^3) \times 10^{-(6 \times 10^{-5})t}$	6.85×10^3	34.90×10^3	0.1961	
4.	450°	$\frac{R_s}{\phi} = (8.75 \times 10^3) \times 10^{-(2 \times 10^{-5})t}$	8.35×10^3	52.45×10^3	0.1590	
5.	480°	$\frac{R_s}{\phi} = (9.00 \times 10^3) \times 10^{-(2{\cdot}08 \times 10^{-4})t}$	5.56×10^3	73.8×10^3	0.0755*	*Fouling, due to Carbon deposition

$$\frac{R_s}{\phi} = A\,10^{-Bt}$$

A, B are constant at a constant temp.

$\phi = P^{0{\cdot}5} - P/_{250}$

t = days

TABLE 4A—RELATIVE ACTIVITY OF CATALYST AT DIFFERENT TEMPERATURES

Temp., °C	Days	Rs/ϕ	Rise of Activity due to Sudden Rise in Temperature
360	44.0	5.20×10^3	1.861 times
390	45.4	9.960×10^3	
390	82.0	7.550×10^3	1.521 times
420	85.0	11.50×10^3	
420	126.0	7.750×10^3	1.500 times
450	127.0	11.6×10^3	

Activation Energy E = 13.88 Kcal/gm mole.

$$R_A = (6.25 \times 10^4)\, e^{\frac{-13.88 \times 10^3}{RT}}$$

Where T is in °K.

TABLE 4B—RELATIVE ACTIVITY OF CATALYST AT DIFFERENT TEMPERATURES

Temp., °C	Relative Activity (R_A) For Same Catalyst Condition	Initial Activity of the Catalyst	
		R_S/ϕ	Remark
360	1.00	12.30×10^3	Experimental
390	1.861	22.90×10^3	Estimated
420	2.840	34.90×10^3	Estimated
450	4.255	52.45×10^3	Estimated

Acknowledgements

The authors wish to thank Dr. K. R. Chakravorty, Managing Director, Fertilizer Corporation of India Ltd. and Sri B. K. Dutta, Addl Supdt. (CRW), for their valuable guidance and constructive suggestions throughout the work. Their thanks are also due to the authorities of FCI Ltd., Trombay Unit for their co-operation during the experiment.

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[Original Mss. received on Feb. 5, 1973]

UDC 541.128.3: 541.117

During the last decade, low temperature CO-conversion catalyst has found widespread application in industry for the production of hydrogen or synthesis gas for ammonia manufacture. The catalyst preparation method has a marked effect on its activity and life. For copper oxide–zinc oxide type catalysts, coprecipitation has been found to inpart them high activity. The amount of copper content of the catalyst influences the activity as well as physical parameters, like surface area, copper crystallite size, etc. There is a sharp increase in the activity of the catalyst with increase in the copper oxide content to about 30 per cent thereafter; the activity increases marginally up to 46 per cent copper oxide, whereafter activity declines.

The life of LT catalyst in industrial converters can be extended by controlling the amount of sulphur and chlorine present in the feed gas. Experiments conducted on sulphur poisoning indicate that tolerance to such poisoning can be improved by changing catalyst formulation. LT catalyst is susceptible to thermal sintering, and generally the catalyst operating temperature is fixed between 200 and 250°C and prolonged operation at higher temperatures causes sintering and permanent deactivation of the catalyst. As such catalyst reduction, which is highly exothermic, must be controlled to avoid temperature runaway; low concentrations of hydrogen in nitrogen are ideal for catalyst reduction.

Factors Affecting the Activity and Life of Industrial Low Temperature Shift Catalyst

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The catalytic conversion of carbon monoxide with steam ($CO+H_2O \rightleftharpoons CO_2+H_2$) is utilized for the production of snythesis gas for ammonia manufacture. The conventional iron-chrome catalyst (HT-catalyst), which is in extensive use in the reaction for the last 40 years, works efficiently in the range 350-500°C. The reaction is equilibrium-limited and higher conversion can be achieved by decreasing the temperature.

Accordingly, attempts were made to develop a catalyst which could work efficiently at lower temperatures. Metallic oxides have been investigated by Ward[1] and it was found that a combination of different metal oxides may have suitable properties for use as a catalyst. Storch[2] studied the combination of cobalt and copper oxides which showed a high initial activity but within a very short time a sharp fall in activity was observed. The first commercial application[3] of LT catalyst dates back to 1930. The catalyst, however, did not find significant commercial use due to its relatively poor life, about 6 months. The catalyst could be subsequently improved and has found widespread commercial application during the last decade.

The two factors that are responsible for the deactivation of the catalyst are thermal sintering and poisoning by small concentrations of impurities such as sulphur and chlorine. In the present study, it has been shown that by correct formulation of the catalyst and proper choice of operating conditions both these factors can be reduced to a considerable extent. Catalyst reduction which greatly influences the catalyst performance has been discussed in details.

Discussion

Advantages: An idea of the principal advantages that can be gained by the use of LT catalyst may be obtained from the following discussion.

Fig. 1 shows the variation of equilibrium carbon monoxide leakage with temperature for a typical gas composition in a naphtha-based ammonia plant. The equilibrium approach for FCI-LT catalyst being about 10°C, carbon monoxide content in the exit LT-converter may be as low as 0.2 per cent. With such low concentration of carbon monoxide, methanation catalyst can be conveniently used for the removal of last traces of

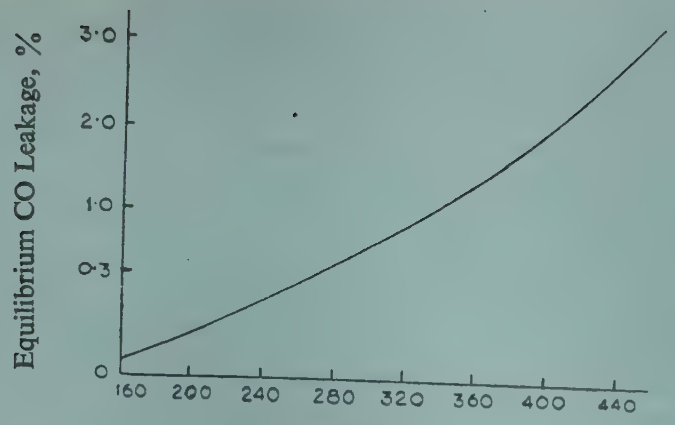

Fig. 1—Variation of Equilibrium of Carbon Monoxide with Temperature.

carbon monoxide and dioxide without involving high purge loss. In recent years, the use of LT-methanation combination has become a standard practice in the design of ammonia plants. The main advantages of using LT catalysts are: (i) additional hydrogen make due to higher conversion of carbon monoxide, resulting in higher amount of ammonia make per unit of feed; (ii) incorporation of methanation for final removal of carbon monoxide, eliminating costlier copper liquor or liquid nitrogen washing; and (iii) lower installation and running cost.

Catalyst Formulations: Catalysts comprising different formulations, like copper oxide–zinc oxide, copper oxide–zinc oxide–alumina, copper oxide–zinc oxide–chromia and copper oxide–zinc oxide–chromia–alumina, have been used in commercial plants. Several workers have studied the different methods of preparation of the catalyst and their effect on its activity and physico-chemical properties.

The preparation by different methods have been shown to produce catalysts having widely different activity[4]. The precipitation pH greatly influences the character of the precipitate and in turn affect the activity of the catalyst. It is seen[5] that copper oxide–zinc oxide (CuO—ZnO) type catalysts can be best prepared by co-precipitating carbonates (along with basic carbonate) of copper and zinc from a solution of their salts.

Copper is the active component of the catalyst and may be supported on high surface area materials, like zinc oxide and alumina. Presence of zinc oxide is considered essential as it preferentially absorbs sulphur, because of the higher value of K_p, and thus protects the copper from sulphiding. For copper oxide–zinc oxide type catalysts, variation of activity with copper content is shown in Fig. 2. The catalytic activity increases sharply up to 31 per cent copper oxide, whereafter there is only slight increase up to 46 per cent copper oxide. Beyond this, there is a rapid decline in the conversion efficiency. It is interesting to note that beyond 46 per cent copper oxide, there is a sharp rise in copper particle size resulting in sharp fall in copper surface area[5]. Constant research for improvement in catalysts has led to the development of a new catalyst having the following percentage composition: copper oxide 23, zinc oxide 20, alumina 42, ferric oxide 8.0 and titania 5. The catalyst is characterized for its higher activity and high sulphur tolerance.

Reaction	Temp., °C	K_p
$Cu + H_2S \longrightarrow CuS + H_2$	220	7.8
$2Cu + H_2S \longrightarrow Cu_2S + H_2$	220	1.2×10^5
$Zno + H_2S \longrightarrow ZnS + H_2O$	220	7.9×10^7

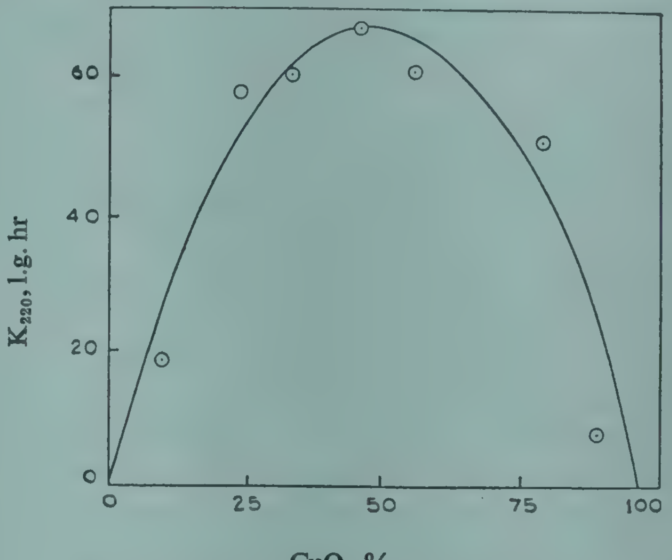

Fig. 2—Dependence of Catalytic Activity on Copper Oxide Concentration

Deactivation: It has been mentioned that factors responsible for catalyst deactivation are thermal sintering and poisoning. In those cases where poisoning is low or absent, the life of the catalyst can be predicted with certainty.

The presence of poisons in the feed stream can arise in various ways. Sulphur in the hydrocarbon from the desulphurization system is the primary source of such poisons. Maloperation of the desulphurization system and failure to detect even very small levels of sulphur leakage may lead to short catalyst life. Reformed gas normally contains much less than 1 ppm of sulphur but higher concentration can occur, during initial reduction operation of H. T. shift catalyst.

The chloride sources include (i) compressor lubricants, (ii) quench water for controlling the temperature of the feed gas; (iii) some type of the refinery gas used as hydrocarbon feed; and (iv) refractories used for vessels.

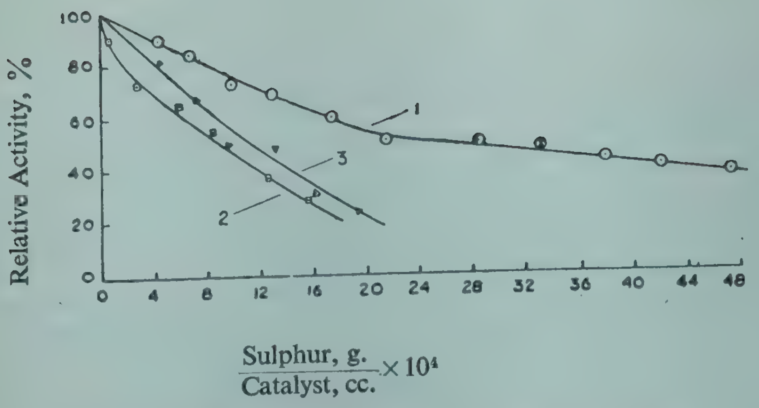

Fig. 3—Dependence of the Loss in Activity with the Weight of Sulphur per Cubic Centimetre of the Catalyst.

1—New Formulation (CuO: ZnO: Al_2O_3 = 1:1.1:1)
2—Catalyst A (CuO: ZnO = 1: 2)
3—Catalyst B (CuO: ZnO = 1: 2)
Reactor Temp., 220°C; S.V.20,000; H_2S in wet gas 5 ppm

Sulphur is the most common and widely known poison for low temperature shift catalyst. Fig. 3 shows the loss in activity of low temperature shift catalyst as a function of g. of sulphur/cc. of the catalyst. The tests were carried out in bench scale reactors under indentical feed and reaction condition to evaluate the extent of loss in activity for the same amount of hydrogen sulphide feed. The poisoning of the catalyst by sulphur compounds is cumulative in nature. Sulphur is quantitatively retained by the catalyst and is not detected in the exit gas. The results clearly indicate that the extent of loss in activity differs widely for different catalyst formulations. The alumina containing catalyst is much superior to the non-alumina catalyst with respect to poisoning. It can be concluded from the results that 0.1 per cent w/w poison could be sufficient to reduce the catalyst activity substantially (about 30 per cent of the initial activity) even with the most tolerant catalyst. Therefore, in order to have the effective life of the catalyst for a reasonable period, the potential sources of sulphur poison must be identified and their introduction into the system eliminated as much as possible using a suitable guard catalyst.

Thermal Sintering: The susceptibility to thermal sintering is a basic property of the catalytic material. As copper is not a very goodrefractory metal (m. p. 1083°C), the catalysts containing copper metal are prone to loss of activity resulting from thermal sintering. The temperature range used for normal operation of low temperature shift catalyst is 200-250°C, where thermal sintering can be largely eliminated by the correct formulation of the catalyst.

The method of preparation has vital role on the thermal stability for this type of catalyst. Studies with different formulations show that for chromic oxide containing catalysts, thermal stability is increased with increasing amount of spinel[6] ($ZnCr_2O_4$). For copper oxide–zinc oxide type catalysts, addition of alumina is said to increase its thermal stability[7]. It has been seen that catalyst having the same chemical composition can have different thermal stabilities. Fig. 4 shows the rate of loss in activity with time on stream for 4 samples having different chemical compositions and methods of preparation. The catalysts A and D having similar chemical composition have entirely different rates of sintering. All the catalysts have been tested under identical operating conditions with poison-free gas in a bench scale reactor. For FCI-LT catalyst, the rate of loss of activity caused by thermal sintering is much less up to 300°C but with prolonged operation at high temperature the catalyst loses a part of its low temperature activity.

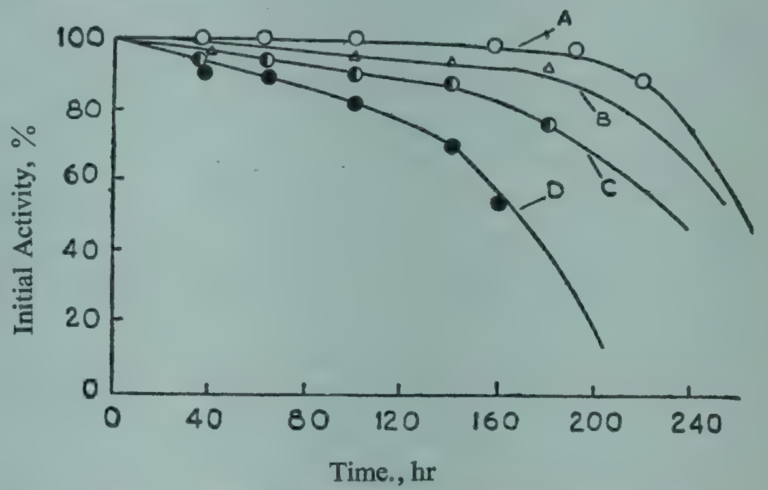

Fig. 4—Thermal Stability of Different Formulations
A. and B Commercial Catalysts (CuO, ZnO, Al_2O_3);
C (CuO, ZnO) Catalyst; D Poorly Formulated Catalyst

Catalyst Activation by Reduction: The catalyst is usually supplied in the oxidized form and is activated by reduction in converters. It can be shown from thermodynamic data that, during reduction only copper oxide is reduced to copper and zinc oxide or alumina remains unchanged. X-ray investigation of the reduced catalyst also confirms this. The reduction reactions are—

Reaction	ΔH **K Cal/mole (at 25°C)**
$CuO + H_2 \longrightarrow Cu + H_2O$	−20.7
$CuO + CO \longrightarrow Cu + CO_2$	−30.5

There are examples of catalyst damage due to overheating during reduction. As such the extent of reaction must be so controlled that the maximum temperature at any part of the catalyst bed does not exceed 250°C. As reduction condition has great influence on the life and activity of the catalyst, reduction must be carried out in a carefully regulated manner.

The catalyst can be reduced at 1-30 atm. pressure using 200-1000 space velocity. A high space velocity is desirable as this ensures better heat distribution and temperature control is easier. The catalyst bed is usually heated at a rate not exceeding 30°C/hr in a stream of nitrogen containing less than 0.3 per cent hydrogen initially. Nitrogen may be replaced by natural gas. As the temperature increases, reduction starts as evidenced by the consumption of hydrogen and rise in bed temperature. The rate of hydrogen feed may be gradually increased, keeping the temperature within specified limits. Finally, as the hydrogen consumption decreases, its concentration may be increased to about 10 per cent until the reduction is completed. It is desirable to reduce the catalyst at as low a temperature as possible. With nitrogen as carrier gas reduction may be completed within 180°C.

Reduction with steam as the carrier gas is not desirable because (1) the activity of the catalyst is about 90 per cent of that reduced in N_2/H_2 stream, (2) surface area of the catalyst has been found to be lower, (3) temperature during steam reduction is usually higher, which results in the loss of a part of the low temperature activity of the catalyst and (4) difficulties associated with the analysis of the hydrogen content makes the control of the reduction process difficult and may lead to catalyst damage.

In an example of reduction of the catalyst in a converter containing 53 M^3 of catalyst, reduction was carried out in a recirculating system at 17 kg./cm^2. pressure using nitrogen carrier gas flow of 12,000 NM^3/hr. The catalyst bed was heated in nitrogen at a rate of 30°C/hr and as the temperature reached 70°C metered amount of hydrogen was dosed till a concentration of 0.15 per cent was built up, whereafter further addition was stopped. As the temperature of the top of the catalyst bed reached 130°C, reduction was initiated, as shown by the slow consumption of hydrogen. After 2 hr. the middle section of the bed also attained 130°C and consumption of hydrogen increased. Hydrogen feeding was resumed at this point and the inlet and exit hydrogen were analysed every $\frac{1}{2}$ hour. As the hydrogen consumption increased further, its flow was also increased gradually the maximum being 130 M^3/hr—and no hydrogen could be detected at the converter exit up to 35 hr after the start of the reduction. Then the rate of hydrogen consumption decreased and its concentration started building up and gradually reached 10.5 per cent at the inlet after another 20 hr whereafter no more hydrogen consumption could be detected confirming the completion of reduction. The maximum temperature at the top, middle and bottom sections of the catalyst bed during the whole period of reduction were 209, 222 and 206°C respectively.

From the above discussion, it is clear that the premature catalyst failure may be due to thermal sintering and poisoning by traces of sulphur and chlorine present in the feed gas. Sintering of low temperature shift catalyst cannot be completely eliminated due to the presence of copper but can be largely reduced by the correct choice of composition and the method of preparation. The results also indicate that the extent of deactivation for the same quantity of the poison is not the same for different catalysts. Thus, the catalyst life in industrial converter can be extended by the proper selection of the catalyst.

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[Original Mss. received on April 24, 1973]

UDC 546.74–31: 541.11.03

The effects of temperature and time of heat treatment on surface area, grain size and pore radius of precipitated iron oxide have been studied in the temperature range 573-773°K. The surface area appears to bear a linear relationship with time and temperature of heat treatment. An empirical relationship, $D^6 = kt$, between grain size and the time of heat treatment at constant temperature has been observed. The activation energy for grain growth has been found to be 17.3 K.cals mole^{-1}. Surface diffusion appears to be the probable mechanism for sintering of iron oxide under the experimental conditions.

Dependence of Physico-Chemical Parameters on Heat Treatment of Iron Oxide

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Introduction

The operational steps in preparation, individually and collectively, influence the surface and bulk properties of intermediates and finished catalysts. Heat treatment is an essential and a critical step in catalyst manufacture. It particularly influences greatly the structural and textural features of the catalyst, which in turn affect the activity and stability of the finished catalyst. In the preparation stage, the constituents of the catalyst are suitably sintered to develop the desired structural and textural character. This sintering is affected almost universally by heat treatment. The mechanism of surface area changes is complicated by the fact that elevated temperatures encourage sintering so that particles in contact weld together because of transport of atoms leading to a reduction of surface area and related changes in the physical parameters.

Iron oxide–chromium oxide type CO-conversion catalyst is generally used for carrying out the water gas shift reaction in commercial plants in the range 573-773°K. Iron oxide is the bulk component in the catalyst. A number of workers[1–5] have studied the effect of heat treatment on iron oxide by heating for a fixed arbitrary period of time at a series of temperatures. Less information in literature is available regarding the effect of time of heat treatment at a particular temperature on the physico-chemical parameters of iron oxide. Since in a commercial plant, both temperature and time are significant for quality and quantity of the product, the present investigation was undertaken to optimize the conditions for heat treatment to develop the desired surface characteristics, and the effects of temperature and time of heat treatment on surface area, grain size and pore radius of precipitated iron oxide have been determined in the range 573-773°K.

It has generally been observed that with the increase in time and temperature of heat treatment, there is a progressive growth in size and increase of average pore radius of iron oxide particles with consequent decrease in surface area. The decrease in the surface area of iron oxide is caused by the sintering of the grains. The extent to which iron oxide particles are sintered depends on the mechanism of diffusion. According to Huttig[6], the rate of sintering depends on the ratio of sintering temperature (T) to the melting point of oxide (T_m). Nicholson[7] has pointed out that the rate of sintering in the region, where surface diffusion is predominant, follows the equation:

$$\frac{dS_t}{dt} = -K_s\,(S_t - S_f).$$

On the basis of these informations and the experimental findings, the present authors have attempted to explain the mechanism of sintering of iron oxide.

Experimental

1. *Preparation of Samples*

In all, five series consisting of 22 samples were prepared in the following manner. The precipitated ferrous carbonate obtained by reacting ferrous sulphate solution with ammonium carbonate was dried in a steam drier at 393°K for 12 hr granulated to −7+12 mesh (BSS) size. The granules, thus obtained, were subsequently heat treated in the electrical furnace for preparing the following samples.

Series A: Heat treated at 573°K for 2, 4, 6 and 8 hours.

Series B: Heat treated at 623°K for 2, 4, 6 and 8 hours.

Series C: Heat treated at 673°K for 2, 4, 6 and 8 hours.

Series D: Heat treated at 723°K for 2, 4, 6 and 8 hours.

Series E: Heat treated at 773°K for 2, 4, 6 and 8 hours.

In series A and E, one more sample in each was subjected to prolonged heat treatment for 24 hours.

2. *Measurement of Physical Parameters*

(A) *Surface Area:* The surface areas of the samples were determined by nitrogen adsorption at −196°C using BET method, taking the molecular cross-sectional area of nitrogen as 16.2 Å.[2]

(B) *Total Pore Volume, Average Pore Radius and Average Grain Radius:* The evaluation of overall volume of pores V, the average pore radius (r_p) and average grain radius (r_g) were determined by methods described elsewhere[8].

Results and Discussion

Effect of Temperature and Time of Heat Treatment on Sintering: Figs. 1 and 2 indicate that surface area decreases with the increase of temperature and time of heat treatment. The greater vulnerability of surface area to shrinkage with increase of temperature compared to that on prolonged period of heat treatment at lower temperature is also clear. It may be interesting to note that a sample cured at any particular temperature for 8 hr has approximately the same surface area when the sample is cured for 2 hr at 50°C higher. This relation appears to hold throughout the range of temperatures studied.

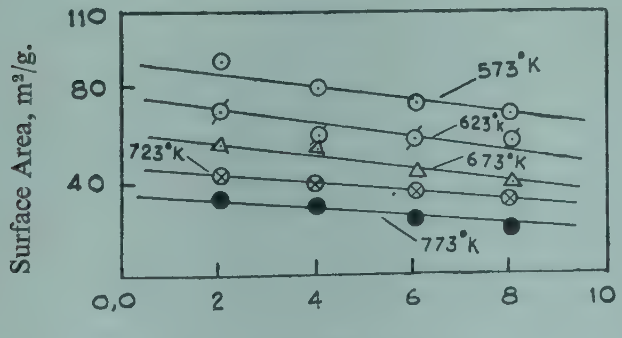


Fig. 1—Plot of Surface Area Against Time of Heat Treatment

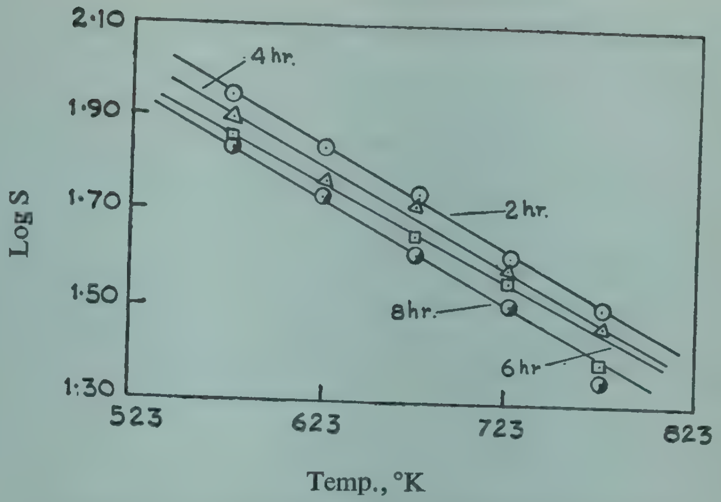


Fig. 2—Plot of Surface Area Against Temperature of Heat Treatment

Fig. 1 shows a linear relationship between surface area and time of heat treatment, whereas with increasing temperature the surface area change is logarithmic. The shrinkage in surface area with the increase of temperature is comparatively rapid initially and then becomes slow. Thus, surface area comes down from 356.0 to 89.0 m²/g., when the temperature of heat treatment is raised from 393 to 573°K. The rapid rate of sintering continues upto 673°K and beyond that the rate of shrinkage becomes comparatively slow with increasing temperature. The effect of prolonged heat treatment on surface shrinkage is evident from the data (Table 1). A sharp fall of surface area of the parent oxide, viz., from 356.0 to 89.0 m²/g., has been observed when the temperature is raised by 180°K, indicating that the fine particles of oxide eventually formed during decomposition are immediately subjected to a fast rate of sintering. Dollimore *et al* [9,10] observed that in case of zinc oxalate and oxalates of

TABLE 1

Sl. No.	Description	Surface Area, m²/g.
1.	Sample obtained on decomposition of ferrous carbonate by heating at 393°K for 12 hr	356.0
2.	Sample 1, cured at 573°K for 24 hr	41.0
3.	Sample 1, cured at 773°K for 24 hr	11.0

heavy metals, the surface area of the oxide is the highest at the decomposition temperature of the salts. In the present investigation, iron oxide obtained by decomposition of ferrous carbonate at 393°K gives the highest surface area. Huttig[6] and Gregg[11] have classified sintering into three processes: (i) adhesion, (ii) surface diffusion, (iii) lattice diffusion or bulk diffusion. According to Huttig,[6] the mechanism of diffusion depends on the ratio of the sintering temperature (T) to the melting point of the oxide (T_m).

Adhesion occurs only at lower temperature and Nicholson[7] has pointed out that when T/T_m is less than 0.2, adhesion is the main mechanism of sintering. From 0.2 to 0.35 surface diffusion is the mechanism and bulk diffusion is operative only above the Tamman Temperature ($T/T_m=0.5$). It is expected that each of these three sintering mechanisms will have a different effect on the rate and extent of change in surface area.

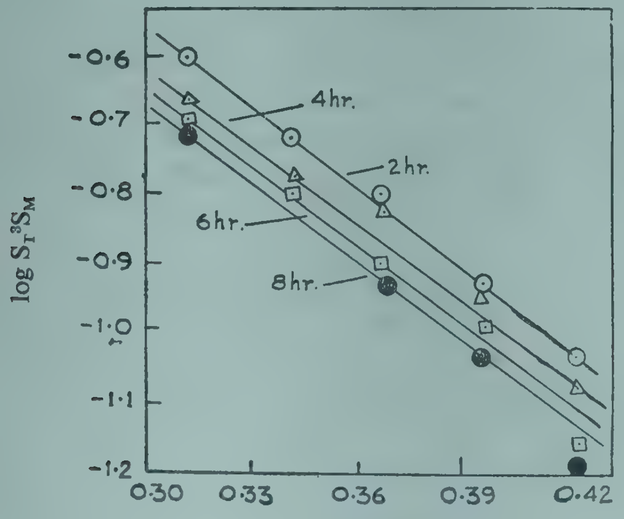
The ratio T/T_m in the temperature range at which the investigation was carried out lies between 0.31 and 0.42. For the heat treatment temperature ranging from 573 to 673°K, the ratio T/T_m lies between 0.31 and 0.36 and here surface diffusion may be the mechanism of sintering as pointed out by Nicholson[7]. The ratio T/T_m at 723 and 773°K are 0.39 and 0.42 respectively. In this region the sintering mechanism may be a combination of surface and bulk diffusion. If surface diffusion is the operative mechanism[10] log (S_T/S_m) will bear a linear relation with T/T_m. It may be seen (Fig. 3) that plots of log (S_T/S_M) against (T/T_m) are linear where S_T is surface area of the oxide at temperature T°K, T_m°K is the melting point of the oxide and S_M is the maximum surface area recorded upon decomposition of the ferrous carbonate from which the oxide is formed. Hence, on the basis of the above results it can be inferred that only a single mechanism, i.e. surface diffusion, is predominantly taking part during sintering of synthetic iron oxide in the region 573 to 773°K. This is further verified by applying the expression of Nicholson[7] to the present results. Nicholson[7] has pointed out that the simplest expression for sintering would be,

$$\frac{dS_t}{dt} = -K_s(S_t - S_f) \tag{1}$$

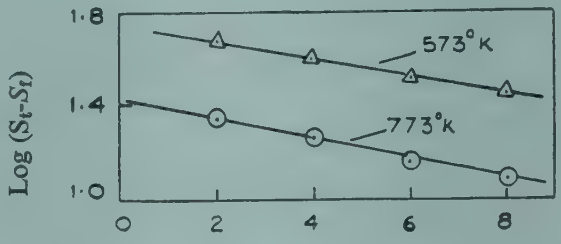
where, S_t and S_f are surface areas at time 't' and the finally attained respectively and K_s is a rate constant.

Hence, $\log (S_t - S_f) = -K_s t + \text{constant}$ (2)

The expression $\log (S_t - S_f)$ is plotted against t (Fig. 4). A straight line relationship in the range 573 to 773°K is clearly evident. This again confirms that surface diffusion is the probable mechanism under the conditions of the present investigation.

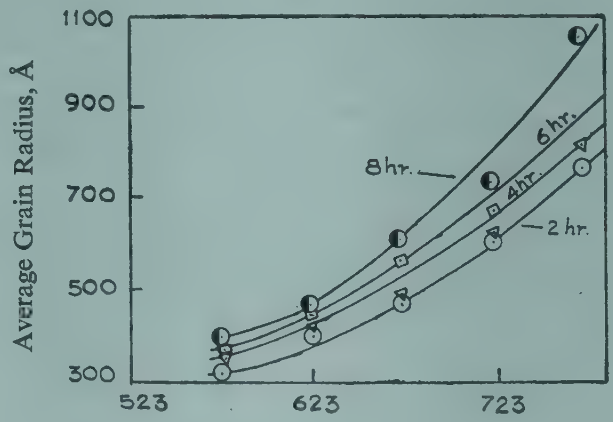


T/T_m
Fig. 3—Plot of Log S_TS_M Against T/T_m



Time, hr
Fig. 4—Plot of Log (S_t-S_f) Against Time

The plots of average grain radius (r_g) and pore radius (r_p) with increasing temperature of heat treatment are presented in Figs. 5 and 6 respectively. It may be observed that r_g and r_p values increase with increasing temperature, increase is faster at higher temperature. Iida[12], Coble[13], Daniels *et al*[14], Nicholson[15], and Brown[16] have shown that grain growth follows the empirical equation, $D^n = kt$,



Temp., °K.
Fig. 5—Variation of Average Grain Radius with Temperature

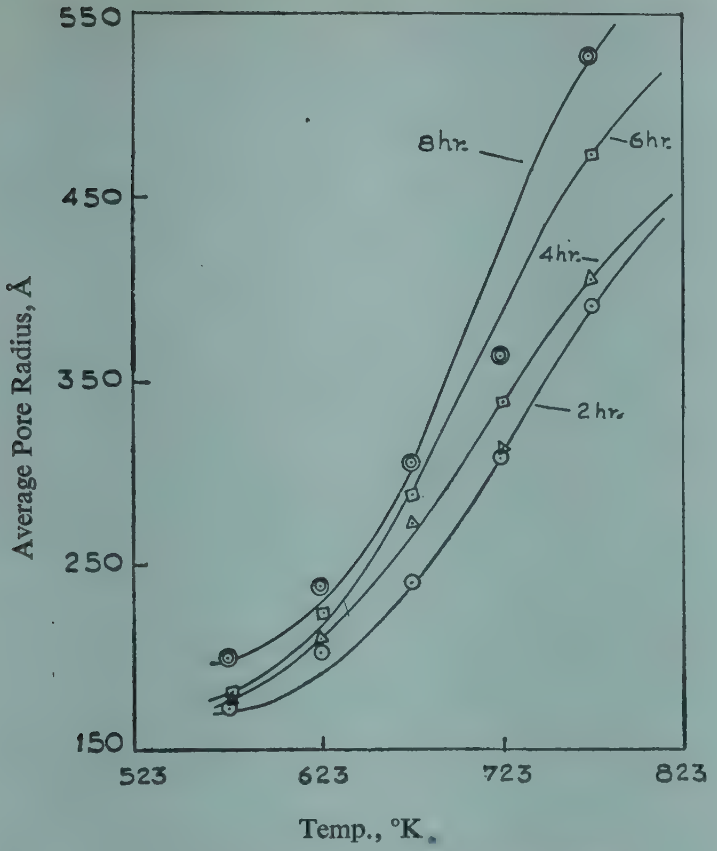


Fig. 6—Variation of Temperature Against Average Pore Radius

where D = average grain diameter, n = constant, k = rate constant and t = time (hour)

The plots of log D against log t (Fig. 7) give straight lines similar to that obtained by Brown[16] for grain growth in case of active nickel oxide. The curves drawn through the points for the respective isotherms (Fig. 7) have slopes varying from 0.16 to 0.21 in the range of the experimental temperature. From these data, the average value of slopes comes out to be 0.17 which has been taken for calculation of the value of n. The calculated value of n from experimental data comes out to be approximately 6. Hence, it seems that in the case of iron oxide the grain growth follows the equation

$$D^6 = kt.$$

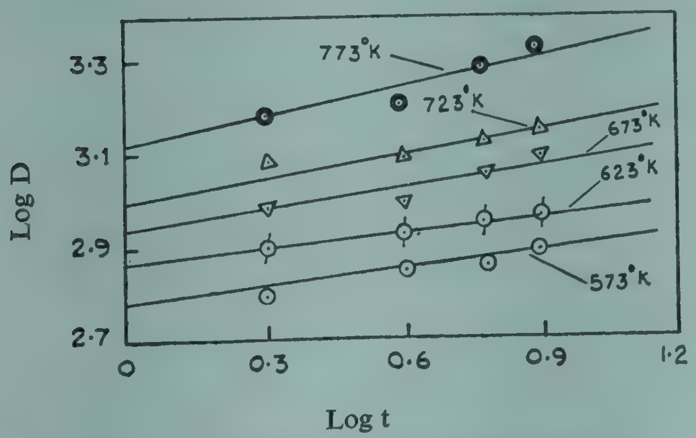


Fig. 7—Rate of Grain Growth of Ferric Oxide

Activation Energy for Grain Growth: For calculation of activation energy for sintering, Arrhenius expression $k = Ae^{-E/RT}$ has been utilised. The intercepts give the corresponding values of 1/n log k directly from the plots of log D against log t (Fig. 7) for different temperatures (T°K).

The value of activation energy has been calculated from the slopes of plots of log k against 1/T (Fig. 8). It is found to be 17.3 K. cals. mole^{-1} in the range 573-773°K. In a similar study[5], the activation energy for iron oxide was reported to be 6.5 K. cals. mole^{-1} in the range 673-1273°K. In general, the energy of activation of a process is inversely proportional to specific rate. It follows, therefore, when the value of E is computed in the range 573°-773°K, the average reaction rate is comparatively lower and hence the value of E becomes higher. Therefore, the value of 6.5 K. cals mole^{-1} as reported earlier[5] over a range 673 to 1273°K, is not unexpected where the rate of grain growth is comparatively faster than in the lower temperature region.

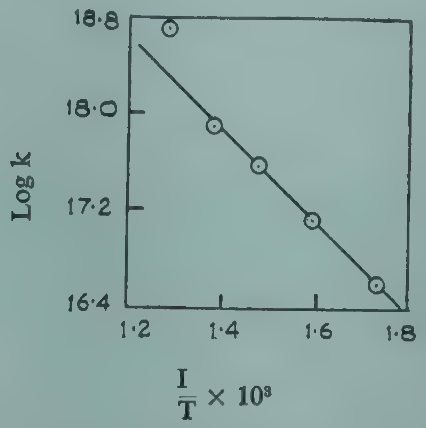


Fig. 8—Arrhenius Plot for Rate of Grain Growth of Ferric Oxide

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[Original mss. received on March 21, 1973]

UDC 541.128: 546.723 – 31

The pore size distribution, surface area, and activity of three commercial shift catalysts (ferric oxide–chromium oxide type) have been determined. The effectiveness factor has been calculated from the pore size distribution data following Wheeler's method. The activity has been found to be dependent on the effective pore area. From kinetic considerations, it has been shown that Knudsen's diffusion predominates in the pore range 90-250 Å radius. The activity is also found to be dependent on the percentage lowering of specific surface area on reduction of the catalyst.

Significance of Pore Size Distribution in Relation to Catalytic Activity of Ferric Oxide-Chromium Oxide Type CO-Conversion Catalysts

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It is known that for a catalyst, greater the extent of surface available to the reacting gases, the better is the conversion. However, surface area is not the only physical parameter which determines the extent of adsorption and reaction. The accessibility of a catalyst surface to reactants is of primary importance in heterogeneous catalysis and is dependent on its pore structure. The pore size distribution can of itself have remarkable effect on the nature and distribution of products. For example[1], in a rapid gas phase reaction as in the oxidation of ethylene to ethylene oxide or oxidation of naphthalene to phthalic anhydride, the presence of large pores is essential to permit the desired product to desorb out of the catalyst readily and thus prevent its over-oxidation.

Topchieva *et al*[2] from their study of the cumene cracking reaction on alumino-silicate catalysts have established that the reaction proceeds in the kinetic and intra-diffusion areas as a function of the pore radii of the catalyst. The pore structure of a catalyst may therefore have a profound effect on the extent of reaction in a catalytic reaction.

In view of this, the present work was undertaken to find out the effect of pore structure of ferric oxide–chromium oxide type shift conversion catalysts on their activity. To get an idea of the available surface, the effectiveness factor was calculated from the pore size distribution data following Wheeler's method[3]. The mechanism of diffusion has also been discussed. The relationship between the activity and the extent of lowering of surface area in the samples after reduction has been examined.

Experimental

The investigation was carried out with three different ferric oxide–chromium oxide type shift catalysts, (A, B & C) of commercial variety. Their surface areas were measured by the B.E.T. method by nitrogen adsorption at $-196°C$. For pore size distribution a mercury pressure porosimeter (Aminco Model 5-7121 SP) having a working pressure range upto 15,000 psi was used. The data for the plots of $\frac{dv}{dr}$ against r were computed from the volume of mercury penetrated at different pressures. The total pore volume was determined by the difference of mercury and helium displacement volumes and the average pore and grain radii by the methods described elsewhere[4].

The activity of the samples was determined in a bench scale reactor similar to the one described earlier[5]. 25 cc. of the original cylindrical tablets were used for this purpose. However, to find out the absolute value of rate constant for the calculation of effectiveness factor, 5 cc. of the catalyst of 0.83-0.99 mm. size was used. The reduction and activity determination were carried out at 350°C using a gas containing about 20 per cent carbon monoxide and rest nitrogen. The steam-to-gas ratio was maintained at 3.0. A dry gas space velocity of 5000 was maintained for activity measurements. Care was taken to ensure that there was no external mass transfer restrictions at this space velocity in both the cases. The rate constant was calculated from the following equation, assuming a first order rate reaction as proposed by Bortolini[6].

$$k_1 = -V(R+1)\ln\left(1-\frac{\eta}{\eta_{eq}}\right)$$

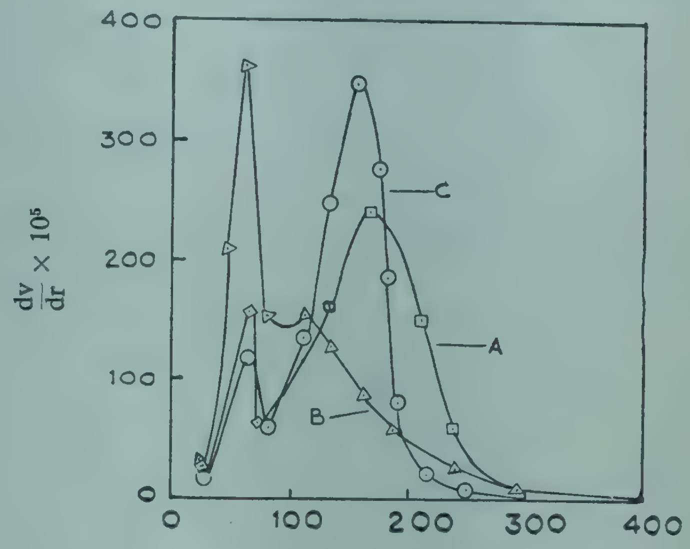
where, k_1 = rate constant cc./hr/g.
V = space velocity cc./hr/g. of reduced catalyst
R = steam/gas ratio
η = percentage conversion.
η_{eq} = percentage conversion at equilibrium.

The reduced samples for surface area and pore size distribution measurements were carefully handled in nitrogen atmosphere to avoid oxidation.

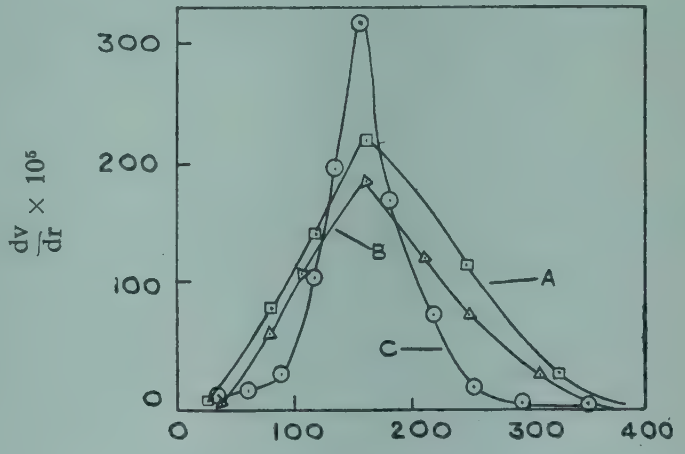
Results and Discussion

The surface area, pore volume, etc. for the fresh as well as reduced samples are given in Table 1.

Figs. 1 and 2 show the pore size distribution curves for the fresh and reduced catalysts. From Fig. 1 it can be seen that for catalyst A there are two distinct peaks —one at 60 Å and the other at 160 Å; for B there is the maximum peak at 60 Å and for C the highest peak is at 160 Å, in addition to one small peak at 60 Å. The pore size distribution of the reduced samples presents some interesting results. In case of all the three reduced samples the peak appears at 160 Å (Fig. 2). A comparison of the distribution curves for the fresh and reduced samples indicates that during the process of reduction there is an increase in average pore radius (Table 1, column 5 and 9). The pores in the lower region disappear resulting in the appearance of bigger pores in the vicinity of 160 Å. The shift of the pore size distribution



Pore Radius, Å
Fig. 1—Pore Size Distribution of Fresh Samples



Pore Radius, Å
Fig. 2—Pore Size Distribution of Reduced Samples

TABLE 1—PHYSICAL PROPERTIES OF FRESH AND REDUCED CATALYST

	Fresh Catalyst				Reduced Catalyst			
Catalyst	Surface Area, $m^2/g.$	Pore Vol., cc./g.	Av. Grain Radius, Å	Av. Pore Radius, Å	Surface Area, $m^2/g.$	Pore Vol., cc./g.	Av. Grain Radius, Å	Av. Pore Radius, Å
1	2	3	4	5	6	7	8	9
A	82.0	0.3292	208	80	44.0	0.3767	538	234
B	61.0	0.2270	25	74	38.8	0.2650	456	173
C	47.4	0.2901	312	122	31.3	0.3273	514	207

spectra to a common zone led to a more detailed study of the pores in this range. Further, an attempt has been made to find out the bearing of activity on these pores.

As has already been pointed out, in a porous catalyst it is not only the total surface but also the accessibility of the pore surface which control the reaction. Hence, in the present work the surface and its availability, i.e. the effective surface within the range of pores, have been assessed. The surface contributed by the pores of 90-250 Å was computed from the pore size distribution data in a manner as communicated earlier[7]. To get a quantitative idea about the available surface, the method as proposed by Wheeler[3] was followed. The following relationships were used for this purpose.

$$E = \frac{\tanh h}{h}$$

where h is a dimensionless parameter which determines the effectiveness factor E.

h is given by

$$h = L\sqrt{\frac{2k}{rD}}$$

where L = average length of a pore, cm.

$$L = \sqrt{2}\,\frac{V_p}{S_x}$$

where V_p is the volume of the catalyst pellet and S_x is the external surface area per pellet.

k = intrinsic rate constant, $cc./sec./cm^2$.
D = effective diffusion coefficient, $cm^2./sec.$

According to Wheeler[3], D may be expressed as

$$D = D_B(1-e^{-D_k/D_B})$$

where D_k and D_B are Knudsens' and bulk diffusion coefficient values. On the basis of the kinetic theory,

$$D_k = 2/3\bar{V}r$$

and $$D_B = 1/3\bar{V}\lambda$$

where $\bar{V}$ and λ are the average molecular velocity, the mean free path of the reacting gas molecule at the reaction conditions and r radius of pore expressed in cm./sec., cm. and cm. respectively. The values of $\bar{V}$ and λ were calculated for carbon monoxide at 350°C and atmospheric pressure.

The values of the effectiveness factor and the computation of the effective surface for the catalysts A, B and C are shown in Table 2, which also gives the tablet sizes and the values of the intrinsic rate constant. Different workers[8–10] have worked on the effect of catalyst size on activity and it has been shown by Popov[9–10] that with catalyst size of 2-4 mm. at 300-400°C the accessibility of total internal surface is 100 per cent and the reaction mechanism falls in the kinetic zone. In the present study a catalyst size of 0.83-0.99 mm. was used for determination of the intrinsic rate constant. It may be said that with this small size, diffusion restriction is eliminated and the reaction falls in the kinetic zone.

The values of the pore surface and the effective surface for each value of pore radius are given in columns 8 and 9 of Table 2. Table 3 gives the cumulative and the total effective surfaces for each catalyst. The activity of the catalyst as determined for the original tablets is given in column 4. It may be seen that the activity decreases with decreasing values of effective surface. As the effective surface is computed from the pore size distribution, it seems that the pore geometry determines to some extent the activity of the catalyst tablets.

From Fig. 2 it may be seen that the distribution curves for pores between 90 and 250 Å are different for the three catalysts. The curve for catalyst A has a broad base whereas for C the base is much smaller. In spite of a higher peak C has a lower effective area. The pores in

TABLE 2—EFFECTIVENESS FACTOR FOR DIFFERENT CATALYSTS

Catalyst	Tablet Size	Intrinsic Rate Constant expressed in cc/sec cm² $k \times 10^6$	Pore Radius $r \times 10^8$ cm.	Effective Diffusion Coefficient cm.²/sec. $\times 10^2$	Dimensionless Parameter, h	Effectiveness Factor E	Pore Surface Contribution, m²/g.	Effective Surface Contribution, m²/g.
A	9 × mm.	7.3	90	3.83	3.08	0.32	9.16	2.93
			123	5.19	2.26	0.43	8.02	3.45
			160	6.66	1.75	0.54	11.75	6.35
			188	7.72	1.50	0.60	4.18	2.51
			250	10.08	1.14	0.70	5.42	3.79
B	8 × 11 mm.	5.9	90	3.83	3.83	0.26	4.00	1.04
			123	5.19	2.81	0.35	10.54	3.69
			160	6.66	2.18	0.45	6.86	3.09
			188	7.72	1.87	0.51	3.94	2.01
			250	10.08	1.41	0.63	6.29	3.96
C	10 × 12 mm.	4.8	90	3.83	4.15	0.24	1.18	0.28
			123	5.19	3.04	0.33	10.11	3.34
			160	6.66	2.37	0.41	11.60	4.76
			188	7.72	2.03	0.47	4.12	1.94
			250	10.08	1.51	0.60	1.00	0.60

TABLE 3—ACTIVITY, EFFECTIVENESS FACTOR & SURFACE REDUCTION FOR DIFFERENT CATALYSTS

Catalyst	Cumulative Surface in the Pore Range 90-250 Å, m²/g.	Effective Surface in the Pore Range 90-250 Å, m²/g.	Activity of Tablets k_1, cc./hr/g.	Reduction in Surface, %	Effectiveness Factor	
					Calculated, E_{cal}	Experimental E_{exp}
A	38.0	19.03	5101.1	46.3	0.433	0.441
B	31.63	13.79	2932.6	36.4	0.355	0.356
C	28.01	10.92	1884.7	34.0	0.349	0.348

A are more uniformly distributed than in C. Therefore a broad pore size distribution throughout the range is found preferable to a sharp peak as obtained in C. The former would offer less diffusion restrictions and result in more accessible surface to the reactant gases.

Besides, the nature of distribution of pores, the ease of formation of the phase Fe_3O_4 may also affect the activity. However, in the present study the ease of formation of the active phase has been assumed to be same for all the samples. In the absence of the history of preparation of the catalysts it is rather difficult to assess this aspect. A detailed study covering the role of electronic factor has been undertaken in this laboratory.

Table 3 column 6 gives the values of the calculated effectiveness factors in the range of pores 90-250 Å for the three catalysts, where

$$E_{cal} = \frac{\text{Total effective surface}}{\text{Total pore surface}}$$

Columm 7 gives the values of experimental effectiveness factor, where

$$E_{exp} = \frac{\text{Activity of tablets}}{\text{Intrinsic activity}}$$

Close agreement between the two values justifies the method of computation of the effective area outlined above and confirms the validity of the assumptions.

The mean free path of carbon monoxide was calculated using the relationship.

$$\lambda = \frac{1}{2^{1/2}\, n\, d^2}$$

where λ = mean free path, cm.
n = number of molecules per cc. of gas at reaction temperature and pressure,
d = molecular diam., cm.

At 350°C and atmospheric pressure, the value of λ for carbon monoxide is found to be 1880 Å.

Now Knudsens' diffusion is the predominant mechanism for mass transfer within the pores when the ratio of pore radius to mean free path of the gas molecules is of the order of 0.1 or less. In the present case it can be seen that, for the range of pores under study Knudsen's diffusion will be the more predominant means of transport for the ferric oxide–chromium oxide type shift catalyst at reaction conditions.

The BET surface areas of the fresh and reduced samples are shown in Table 1. A decrease in surface on reduction has been observed for all three catalysts. But the extent of decrease in surface area varied from sample to sample. For 'A' this reduction is 46.3 per cent where as for sample 'C' it is 34.0 per cent (Table 3, column 5). But it is interesting to note that the activity of A was the highest and that of C lowest. Thus, it appears that the sample which loses the maximum percentage of surface on reduction is the most active. During reduction, the ferric oxide is converted to Fe_3O_4, which is the active form and this change is accompanied by a lowering of the surface. The Cr_2O_3 which is a promoter remains unaffected. A relationship between the reduction in surface and activity of iron oxide was observed by Uchida[11]. He showed that greater the decrease in the surface, greater was the activity. Hence, it appears that during the transformation of ferric oxide to Fe_3O_4, it is not only the total surface that is responsible for activity but also the way in which the active sites are created.

The process of transformation of ferric oxide to Fe_3O_4 is accompanied by an increase in grain size (Table 1, columns 4 and 8), which gives more intergranular voids as is reflected in the increased pore volumes (Table 1, columns 3 and 7).

Acknowledgement

The authors wish to thank Shri D. K. Ghorai for his assistance in this work.

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[Original mss. received on March 18, 1973]

UDC 5.84: 546.284–31: 541.182.5

The development of a new versatile and economic gas chromatographic support by amino-thermal treatment of hydrofluoric acid-treated silica gel has been reported. The pH of the support was ~5 and the surface area ~75m²/g. Studies have been carried out on the gas-solid (GSC) and gas-liquid (GLC) chromatographic behaviour and physico-chemical properties of the solid support, and the decrease in heterogeneity of pore geometry, surface area and surface chemical nature have been discussed. The maintenance of peak symmetry for both polar and non-polar solutes is the special feature of the developed solid support and is responsible for its versatile nature. The support was found to exhibit better performance with respect to hydrofluoric acid-treated silica gel prepared earlier in this laboratory for elution of hydrocarbons, oxygenated and some halogenated derivatives as well as for separation of their mixtures. Its GSC and GLC properties have been compared with those of standard supports like Chromosorb-P and Chromosorb-W (Applied Science Corpn., U.S.A). The temperature co-efficient for retention indices (dI/dT) indicated a slight polarity of the support in comparison to Chromosorb-W.

Studies on Modified Silica Gel for Use as Solid Support in Gas Chromatography

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Recent advances in separation techniques in the field of gas chromatography have resulted in more refinements to the separation processes utilizing, amongst other factors, the various support properties. Development of solid supports very near to an economic and ideal one from indigenous sources, like silica gels, alumina, etc., exploiting their heterogeneous structural and chemical nature has been reported earlier[1–5].

In earlier studies[2], silica gel was modified with transition metal salts and thermal treatments, thus reducing its surface area and widening pore dimensions when metal ions were exchanged for hydroxylic protons of silica gel with subsequent dehydroxylation. But support activity was still present and varied with metal ion concentration to silica gel. Further studies were directed towards modifying silica gel with hydrofluoric acid under specified conditions, which gave a support with similar surface properties as the salt-thermal modified one. Residual activity which still persisted was accounted for as due to the bonding of fluoride with silicon during the hydrofluoric acid treatment of silica.

The present communication deals with the studies carried out on the solid support prepared by amino-thermal treatment of hydrofluoric acid-treated silica (SiO_2-HF-NH_3). It has been assumed that whatever residual free fluorine is left after the first treatment is transformed into an ammonia salt and this is subsequently removed by total evaporation on its ignition. Further, the bonded fluoride is liberated by ammonium hydroxide on exchange with SiF, the resultant ammonium flouride is removed on ignition transforming SiOH into Si-O-Si. It is, therefore, apparent that the treatment removes fluorine leading to the formation of a neutral support.

Experimental

Indigenous commercial silica gel was purified by classical method and dried at 180°C for 7 hr. This was modified with a mixture by hydrofluoric and sulphuric acids under specified conditions and washed with water for complete removal of sulphate ions. The modified silica was dried at 140°C for 7 hr and was further treated with dilute ammonia solution and again dried at 140°C for 7 hr. The dried product was ignited at 900°C for 7 hr. The details of the preparation of the support is sought to be patented.

The physical properties of the modified gel were studied as set forth in earlier papers[1,2]. Aerograph Hy Fi 600 D with flame inoization detector was used for gas chromatographic studies with copper columns of dimension 5′ × 1/8″ unless mentioned specifically otherwise. Hydrogen was used as the carrier gas. The columns were packed by the conventional methods with various supports of uniform mesh size, i.e. 60-100 (BSS), for GSC studies and with supports coated with 10 per cent w/w stationary phase for GLC studies. Squalane and tricresyl phosphate, used as the stationary phase, were procured from BDH and standard supports Chromosorb-P and Chromosorb-W (acid washed silanized) from Applied Science Corpn, USA. For determination of retention index, the solute was always injected along with its two corresponding normal paraffins. Precision sampling syringes were used for injecting 0.1 μl liquid samples. The data reported were the averages from triplicate runs.

Results and Discussion

A comparative study of new support SiO_2-HF-NH_3 with respect to SiO_2-HF and Chromosorb-W is given in Table 1. It has been found that the bulk density of the support is appreciably low and its liquid loading capacity is high. The pH of SiO_2-HF-NH_3 in aqueous suspension is higher in comparison to SiO_2-HF. The H.E.T.P. value for n-nonane is also of the same order as that of a standard support coated with squalane. The surface area and pore dimension were measured qualitatively by the method standardized in this laboratory[6].

Gas-Solid Chromatographic Behaviour: Various types of solutes ranging from hydrocarbons to oxygenated compounds were run under identical conditions of temperature and pressure over different types of supports. The comparison among the supports was made relative to uncorrected retention times of n-pentane (Table 2). The support SiO_2-HF-NH_3 possesses relative retention higher for n-paraffins and lower for cyclic, olefinic and aromatic hydrocarbons with sharp peaks in comparison to other supports. The orders of elution for the oxygenated compounds in all the supports were not identical; alcohols, though retained in SiO_2-HF, are eluted much earlier on the support SiO_2-HF-NH_3 as compared to others. Ethyl acetate was found to have higher retention than ether in all the supports used. It was also observed that the tailing of the oxygenated compounds was high for the SiO_2-HF support and much less for SiO_2-HF-NH_3 and Chromosorb-P supports.

TABLE 1—PHYSICAL PROPERTY COMPARISON OF DIFFERENT SUPPORTS

	SiO_2-HF-NH_3	SiO_2-HF	Chromosorb-W
Colour	White	White	White
pH	5.8-6.4	2.8-3.1	8.10
Bulk Density, g./cc.	0.58	0.50-0.67	0.24
Liquid Loading Capacity, w/w %	35	17-46	30
Surface Area, m²/g.	75[b]	23[b]	1-3.5[a]
Pore Diameter, Å	350-750[b]	760[b]-1360	80,000-100,000[a]
H.E.T.P., for n-Nonane cm.	0.12	0.12	0.11

[a]: from Manufacturer's literature

[b]: calculated as mentioned in Reference 6.

TABLE 2—COMPARATIVE RELATIVE RETENTION (UNCORRECTED) OF DIFFERENT SOLUTES IN GSC STUDY ON DIFFERENT SUPPORTS AT 100°C, 20 PSI

	SiO_2-HF-NH_3	SiO_2-HF	Chromosorb-P
n−Pentane	1.00	1.00	1.00
n−Hexane	1.60	1.20	1.18
n−Heptane	2.60	1.43	1.38
n−Octane	4.30	1.70	1.60
n−Nonane	7.09	1.96	2.05
Cyclohexane	1.39	1.28	1.16
Cyclohexene	2.17	1.51	1.36
Hexene-2	1.74	1.39	1.66
Benzene	1.91	1.79	1.70
Toluene	3.78	3.05	3.40
2,2,4 Trimethyl Pentane	3.13	1.51	1.56
2,3,4 Trimethyl Pentane	3.69	1.51	1.56
2,2,5 Trimethyl Hexane	5.43	1.94	1.86
1 *cis* 2 Dimethyl Cyclohexane	3.91	1.58	1.66
1 *trans* 2 Dimethyl Cyclohexane	3.91	1.58	1.66
Methanol	2.44	Not eluted	3.10
Ethanol	5.04	Not eluted	8.80
Diethyl Ether	10.99	5.82	1.66
Di-isopropyl Ether	25.56	—	2.13
Acetone	10.67	21.82	4.23
Ethyl Methyl Ketone	23.12	—	—
Ethyl Acetate	19.56	36.85	5.26
Dichloromethane	0.978	1.17	1.16

Gas-Liquid Chromatographic Behaviour: The GLC behaviour of a support coated with a neutral stationary liquid phase, e.g. squalane, can best explain its polarity in comparison to a standard one when studied with a variety of solutes. The accuracy of index value which is preferred suitable for the comparison of two supports, is ± 4 units since the main handicap is with temperature control of the oven (± 2°C). The elution characteristics of solutes were observed with the support SiO_2-HF-NH_3 in comparison to SiO_2-HF and Chromosorb-W, each coated with 10 per cent w/w squalane, and variation of index values for solute to solute was more prominent with the oxygenated compounds, e.g. alcohols, acetone, ethers and acetate. A shift of more than 325 units in index values was found for the oxygenated compounds relative to standard support, which indicates a specific property of the support for the oxygenated compounds and this may be used for separation of complicated mixture containing alcohols, ketones, ethers, esters and hydrocarbons on a single phase. The repercussion of support activity over non-polar and polar hydrocarbon solutes has been shown in Table 3. When coated with a neutral phase, the support polarity has not been reflected to any appreciable extent on the elution of non-polar solutes but is more pronounced on the polar solutes. Thus on the one hand, the support SiO_2-HF-NH_3 can serve the purpose for the usual separation of mixtures of hydrocarbons containing saturated, unsaturated, branched, aromatic and cyclic compounds and on the other hand it can help in the separation of mixtures of hydrocarbons and oxygenated compounds using the same neutral phase. This separation efficiency was not possible with available standard supports and is the special feature of the new developed support.

TABLE 3—COMPARATIVE INDEX VALUES OF DIFFERENT SOLUTES ON VARIOUS COLUMNS AT 100°C, 20 PSI

Solutes	SiO_2-HF-NH_3 Coated with 10% w/w Squalane	Chromosorb-W Coated with 10% w/w Squalane	Chromosorb-W Coated with 10% w/w TCP
Cyclohexane	652	675	708
Cyclohexene	692	684	758
Hexene-2	616	606	642
Benzene	670	663	821
Toluene	781	759	927
2,2,4 Trimethyl Pentane	700	696	679
2,3,4 Trimethyl Pentane	762	759	759
2,2,5 Trimethyl Hexane	787	781	760.5
1 *cis* 2 Dimethyl Cyclohexane	831	843	886
1 *trans* 2 Dimethyl Cyclohexane	805	815	847
Methanol	622	311	768
Ethanol	729	395	733
Diethyl Ether	800	486	581.5
Di-isopropyl Ether	875	587	644
Acetone	767	438	716
Ethyl Methyl Ketone	871	—	795
Ethyl Acetate	846	560	754

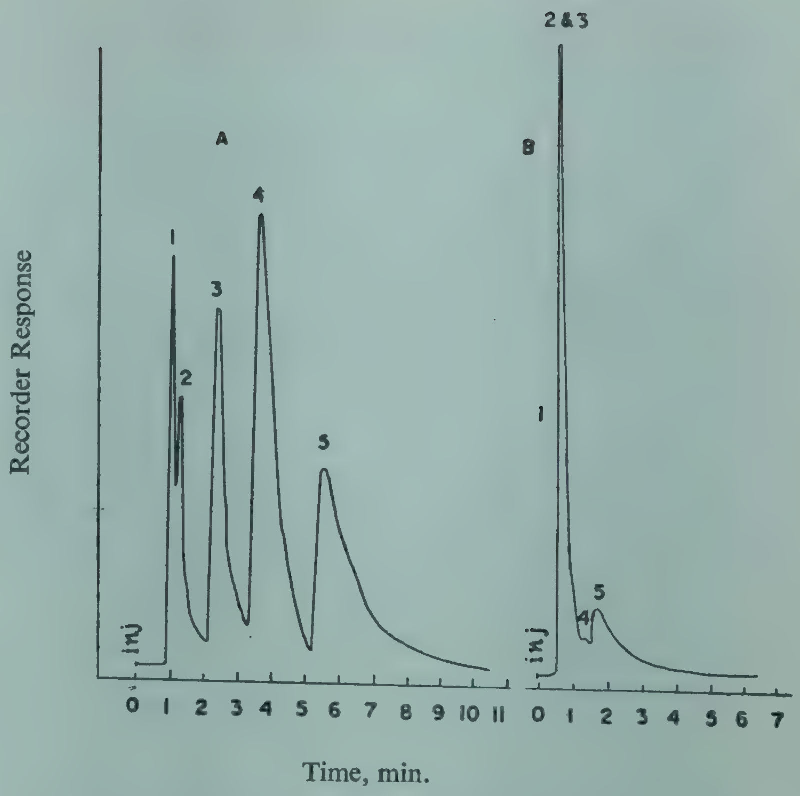

Fig. 1—Comparative Separation Efficiency of Synthetic Mixture of SiO_2–HF–NH_3 (A) and Chromosorb-P (B), both Coated with 10% w/w Squalane at 80°C, 25 PSI, Hydrogen as Carrier Gas and Sample 0.1 μl.

1. Methanol, 2. Formaldehyde 3. Ethanol, 4. Acetone, 5. n–Propanol.

In order to test the separation efficiency of the new support (SiO_2-HF-NH_3) and keeping in view its specific property, a synthetic mixture of formaldehyde, methanol, ethanol, no-propanol and acetone was prepared and separation carried out by gas-chromatography over Chromosorb-P and the new support, both coated with 10 per cent w/w squalane. The separation efficiency of the new support over Chromosorb-P is fully established as shown in Fig. 1.

TABLE 4—EFFECTS OF SUPPORT ACTIVITY ON TEMPERATURES CO-EFFICIENT OF RETENTION INDEX

Solute	dI/dT from 10% w/w Squalane		
	SiO_2-HF-NH_3	SiO_2-HF	Chromosorb-W
Cyclohexane	0.10	0.26	0.23
Cyclohexene	0.30	0.16	0.25
Benzene	0.20	0.14	0.24
Hexene-2	−0.10	−0.10	0.036

Activity Coefficient: The temperature co-efficient of retention index $\left(\frac{dI}{dT}\right)$ method[3] was used for the measurement of relative support activity with respect to Chromosorb-W and SiO_2-HF using various types of hydrocarbons. The dI/dT method is very sensitive to a slight difference in property either in the stationary phase or in the support. Table 4 gives an idea of the activity of the support with respect to Chromosorb-W as standard and wherein the neutral phase squalane was common for all the experiments.

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[Original mss. received on March 22, 1973]

UDC 66.045: 582.232

The problem of the growth of algae in industrial cooling towers has been studied and a very effective and economical method for its control has been developed. Sodium pentachlorophenate has been found to be an efficient algicide if properly applied. The earlier unsatisfactory results obtained by applying this algicide in the circulating water have been attributed to the difficulty in maintaining an effective concentration of about 10 ppm. of this chemical in water continuously for 5-6 days. The present results have revealed that lesser period of contact or still lesser concentration of the algicide has only partial effects.

The application of about one per cent solution of sodium pentachlorophenate by spraying on the affected areas of cooling towers and the isolation of those areas for 2-3 hr. has been found to be very effective. The requirements of the algicide by this method are only 2-5 per cent of that necessary for maintaining 10 ppm. of its concentration by water application. The method is also less time-consuming and has a very little effect on the increase of chloride contents of the cooling tower water.

A Method for Effective Control of Algae in Cooling Towers

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In many industries large volumes of water are generally used for cooling purposes in various ways. The hot water coming out from plants is cooled in cooling towers and is recirculated again. These towers, generally of open recirculatory type with induced or natural drafts, are installed in open spaces having access to direct or diffused sunlight. The water circulated through these towers also contains traces of phosphates, calcium, nitrogen and other inorganic nutrients. As atmospheric carbon dioxide is always available, the environment around the cooling tower is rendered most suitable for the growth of some species of algae. In many towers, heavy algal growths are often noted, which not only lowers the efficiency of the towers but the dislodged algal masses carried by the circulating water creates problems by being deposited in the heat exchanger surfaces and in the packings of the scrubbing towers.

Most of the industries using cooling towers are aware of this problem and the use of different types of algicides is in vogue. Chlorine is commonly used for the control of growth of this algae. It is applied continuously at very small doses with shock dose of high concentrations at intervals. Sodium pentachlorphenate is also used in some cases by direct dosing in the circulating water.

It has been observed that in most of the cooling towers of fertilizer industry, this practice has in fact only some limited effects on the growth of algae and the problem is as acute as ever. Hence, the necessity of a systematic study was badly felt and as a result the present investigations were undertaken. The observations reported in this paper are confined to the cooling towers of the FCI'S fertilizer factories at Sindri and Durgapur.

Methods and Materials

A basal medium (MB) containing 0.3 ppm. of phosphorus as disodium hydrogen phosphate, 0.5 ppm. of potassium as potassium chloride, 8 ppm of nitrogen as sodium nitrate, 0.29 ppm of Ca as calcium chloride, 0.23 ppm of magnesium as magnesium sulphate was used for growing algae under fluorescent light. For the growth of algae on wood pieces, sodium pentachlorophenate was allowed to drop slowly from a 5 lit. aspirator bottle fitted with glass jets on wood blocks held in an enamel tray under fluorescent light.

The plant observations and experiments were carried out in some of the cooling towers at Sindri and Durgapur plants of the FCI Ltd.

Results and Discussion

The cooling towers of the above two plants were kept under observation and the growth characteristics of the algal species recorded. It has been noted that algal masses growing in cooling towers are mainly of blue-green type consisting of two distinct species of *Oscillatoria.* At the earlier stages of growth, the colour of the mass is mainly blue-green and only one variety is noted. In course of time, however, a 'dark brown' variety appears, gradually becoming predominant over the earlier blue green one. Initially, the algal masses form a very thin layer on wooden or concrete support but in course of time this tends to thicken up and ultimately a mat-like layer of 2-10 mm. thickness is formed (Fig. 1). Sooner or later these are dislodged from the support and are carried away by water.

Culturing of Algal Species: The species of algae, specially the brown one, grow easily in presence of the cooling tower water under fluorescent light. After some initial trials, a synthetic basal medium has been evolved. The inoculum after incubation for a few hours first sticks to the bottom of the *petri* dishes and then gradually spreads more or less uniformly outwards. Younger masses will always stick to the bottom but the older ones may partially float on the liquid surface after 4-5 weeks. If the medium in dishes is replaced frequently by fresh ones, the growth continues rather indefinitely.

Control of Algae by Algicides in the Laboratory: After

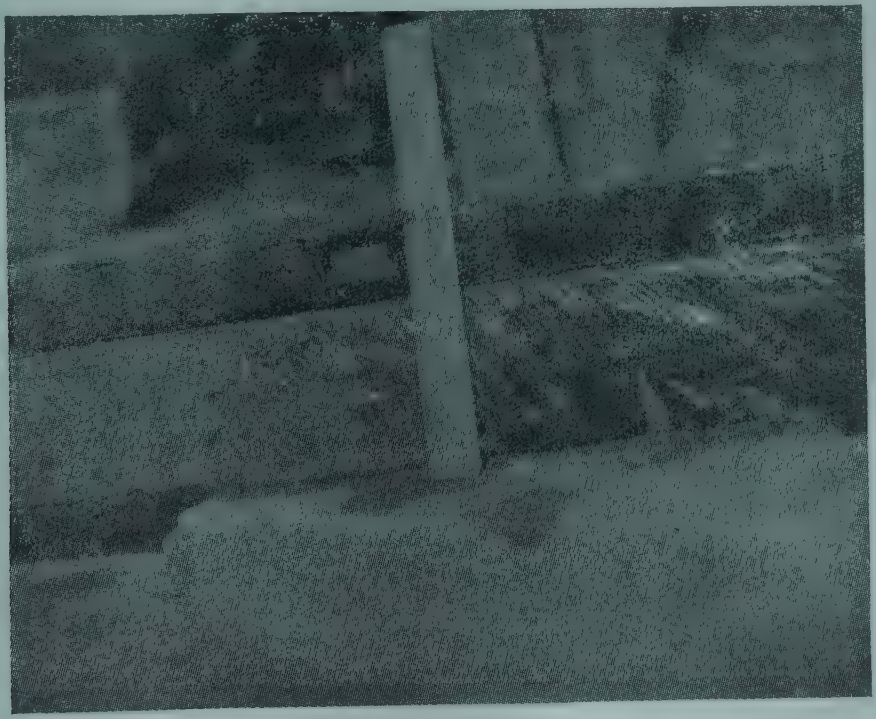

Fig. 1—Wooden Planks Showing Algal Growth.

successful culturing of the organisms under controlled conditions, some algicides were tested for their control. As some commercial brands of sodium pentachlorophenate are already being used in some industries, studies to test the effectivity of these were made.

It may be seen (Table 1) that no growth of algae was noted in basal medium containing 10 ppm. of sodium-pentachlorophenate (Na-PCP).

TABLE 1—GROWTH OF *Oscillatoria* IN 50 ml. BASAL MEDIUM IN *Petri* DISHES

Incubation Period, week	BM + O Control	BM + 10 ppm Na-PCP	BM + 20 ppm Na-PCP
1	*+	(–)	(–)
2	+++	(–)	(–)
4	+++	(–)	(–)

* + Growth evident, +++ = Heavy growth, (–) = No growth.

The inhibition of growth in petri dish cultures by a low concentration of sodium-pentachlorophenate was encouraging and hence the next course was to explore the possibility of controlling the growth on cooling tower wood kept moist by dropping nutrient solution (Tables 2 and 3). It may be seen from Table 2 that the immersion of wood in concentrated solutions of sodium-pentachlorophenate is not effective in controlling the growth on it if the chemicals are subsequently allowed to get washed down.

But if the solutions containing 10 ppm. of algicides are allowed to trickle over the algal masses on wood blocks continuously for a few days (Table 3), the effect is quite spectacular.

Within 2-3 days of treatment, visible signs of discoloration of algal masses on wood blocks were noted when solution containing 10 ppm of the algicide was used and the dead masses were gradually dislodged from the wood surface in 5-6 days, giving the wood a more or less clean appearance.

TABLE 2—GROWTH OF *Oscillatoria* ON WOOD BLOCKS

Treatment	Observation after 7 Days
A. Wood blocks kept immersed in 100 ppm of Na-pentachlorophenate solution for 96 hrs, and then washed in running tap water for 24 hours before use.	Heavy growth
B. Wood blocks untreated	Heavy growth

TABLE 3—GROWTH OF *Oscillatoria* ON WOOD BLOCKS

	Solutions Added Drop-by-Drop on Wood Blocks (Observation after 7 days)		
	BM + O	BM + 5 ppm of Na-PCP	BM + 10 ppm Na-PCP
1. Wood blocks freshly inoculated	Heavy growth	Slight growth	No growth
2. Wood blocks with heavy growth of algae	Heavy growth	Partially killed	Killed and washed down

The above observation led the authors to the conclusion that sodium pentachlorophenate is quite effective in killing the existing masses of algae on wood surfaces if the organisms are exposed to water containing 10 ppm of sodium pentachlorophenate continuously for 5-6 days.

This explains why the earlier practice of dosing sodium pentachlorophenate in water at weekly or fortnightly intervals was not effective. Under the plant conditions, losses of cooling tower water through purging, leakages and evaporation are made up by adding fresh water continuously. Hence, it is difficult to maintain the desired concentration of the algicides for 5-6 days by one application per week. This can be possible only by continuous addition of the calculated amount of algicide along with makeup water. In cooling towers with $100M^3$/hr makeup water the chemical requirements for raising the algicidal concentration to 10 ppm of the makeup water only will be about 18 kg/day and hence 108 kg for six days. It was noted earlier that the addition of a similar quantity of sodium pentachlorophenate once a week might increase the chloride contents of the same cooling tower water and effective control of algae growth was not very satisfactory (Authors' unpublished plant observation).

In some types of cooling tower as are existing in the Sindri factory, a part of it harbouring heavy algal growth does never come in direct contact with the water treated with algicides but is moistened by water vapour arising from hot water flowing through the channels. Under the circumstances, any concentrations of algicides maintained in water will not be effective at all for killing the algal masses growing far away from the channels.

Thus, though the results of the experiments made it clear that continuous addition of sodium pentachlorophenate to maintain about 10 ppm concentration is quite effective against algal species noted in cooling towers, some suitable methods of application for bringing the organisms in direct contact with the algicides must be evolved.

For this purpose, the results of experiments shown in Table 4 have been found very suggestive. It can be seen from the above table that while lower concentrations (10 ppm) of this algicide are effective only after prolonged exposure of 5-6 days, higher concentrations may have immediate effect. Hence, it was decided to apply concentrated algicidal solution on affected spots by spraying. Some experiments were, therefore, conducted by spraying 1 per cent solution of sodium pentachlorophenate in the cooling towers of Sindri factory and the cells were kept isolated for 2-3 hr after application specially during the morning hours. During these trials, it was observed that 70-80 lit. of 1.0 per cent solutions are generally sufficient for spraying all the affected areas of each cell. The results were also very satisfactory even after the first application, only some portions showing heavy growth required a few repeated sprayings at quick intervals for complete elimination.

TABLE 4—EFFECT OF CONCENTRATION OF SODIUM PENTACHLOROPHENATE ON THE ALGAL MASS ON WOOD BLOCKS

(Solutions were allowed to trickle down the wood blocks continuously.)

Conc., ppm	Discoloration of the Algal Mass	Remarks
0	No effect	No effect
10	5-6 days	Algal mass turns greyish yellow gradually.
100	-do-	-do-
1000	2-3 days	-do-
10000	2-4 hours	Algal mass turns dull red in 2-4 hours
20000	immediate	Algal mass turns red immediately after application

After the first application of the algicides in these cooling towers, regular observations were taken and the initiation of fresh growth in the degasifying cooling tower was noted after 14-16 days. In most of the cells of the power house cooling towers, however, fresh growth was noted after 25-30 days.

As soon as the fresh growth was noted, a second dose of 1.0 per cent solution of the algicide was applied and the process was repeated. It has been found that by this process of spray application of sodium pentachlorophenate at intervals of 2-4 weeks, the algal growth can be completely kept under control.

Conclusion

It may be concluded from the above discussions that 10 ppm of sodium pentachlorophenate is quite effective in killing and preventing fresh growth of algae. But this requires an exposure of the organisms to the algicidal solution for about 5-6 days. Under plant conditions, the loss of water due to purging, leakage and evaporation is made up continuously. Hence, to maintain the algicidal concentration to a more or less constant level, continuous addition of chemicals is also necessary. For a cooling tower having 40 M^3/hr makeup water, the normal chemical requirements for maintaining this concentrations in added water will be about 40-50 kg. of sodium pentachlorophenate for one application lasting for 6 days.

On the other hand, for effective spraying of all the regions of a cell showing algal growth 1 kg of the chemical dissolved in 100 lit. has been found to be sufficient. Even if some cells may require repeated spraying, normal requirements are not going to exceed 2 kg. any way. Hence, a cooling tower with 1 cell will require 1-2 kg. of the algicides for the first application and the quantity is likely to be less in the subsequent ones.

The most important fact about this method of application is that a very quick effect is achieved and in addition, the chemical requirement is also only 2-5 per cent of the earlier method. This has got other advantages as well. In the case of water application of the algicides, the whole cooling systems are exposed to 10 ppm of this strong chemicals at least for 6 days by continuous addition of the chemical. As sodium pentachlorophenate decomposes into chlorides in presence of sun-light (Authors' unpublished data) the chloride content of water is likely to go up. This prolonged treatment will also require constant vigilance on the part of the plant operators. In case of spray application, however, one cell of cooling tower can be sprayed in 30-40 min. As the chemical sprayed is much less in quantity, the maximum concentrations of this algicide that can be built up in water even if the whole algicides are washed down after commissioning the tower will never exceed 2-3 ppm with negligible chloride increase in waters.

Thus, from the results of investigations carried out in the laboratory as well as in the plants, it can be concluded that the application of 1 per cent solution of sodium pentachlorophenate by spraying on the affected areas of industrial cooling towers, is much more effective, less time-consuming and economical.

Acknowledgements

The authors' wish to record their thanks to Sri B. K.

Dutta, Addl. Superintendent (P & D) for his active interest in this work and for offering suggestions during the preparation of the mss. Thanks are also due to Sri T. V. Doraiswamy, Addl. Superintendent (Production), Sri M. M. Babuta, Addl. Superintendent (Power House), Sri Arun Mukherjee, Asst. Supdt. (Power House), Sri M. S. Shastri, Plant Manager, Sulphate Plant, Sri K. S. Prasad, Plant Manager, Ammonia Plant, Sri Ranjit Dey, Production Engineer, Power House and Sri B. R. Rao General Foreman of FCI Sindri Unit and Sri J. Chowdhury, Addl. Chief Mechanical Engineer and Sri Sushil Chatterjee of Durgapur Unit for their help and cooperation during the experiments in their respective plants.

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[Original mss. received on March 17, 1973]

UDC 541.18: 532.7: 549.222: 546.175.35

The reactions of three different rock phosphates, viz. Jordan, Nauru and Jhamarkotra, with nitric acid of different concentrations have been carried out at various temperatures. It has been found that in the beginning the reaction is very fast and vigorous with all the rocks and more than 70 per cent of the P_2O_5 present in rocks becomes available within five minutes of the addition of rock to acid. The kinetics of the reaction has also been studied by taking out samples at different intervals of time and analysing for their soluble P_2O_5 contents. The samples were immediately frozen in ice before analysing in order to arrest the reaction at that particular time. It is found that each rock has optimum nitric acid concentration at which maximum decomposition occurs. The reaction between rock phosphates and nitric acid is of first order as the graph obtained after plotting log $\frac{a}{a-x}$ against time is linear. The decomposition reaction also obeys Arrhenius equation because the plot of log K against $\frac{I}{T}$ is also linear. It is observed that the reaction with Nauru and Jhamarkotra rocks is faster than that with Jordan rock.

Nitric Acidulation of Rock Phosphate—Kinetics of the Reaction between Rock Phosphate and Nitric Acid

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The solid-liquid reaction between rock phosphate and nitric acid is the basis of the manufacture of a number of NP/NPK complex fertilizers. This process of manufacture of complex fertilizers has been gaining ground in sulphur importing countries, like India, where feedstocks for ammonia production are available at reasonable prices. Since 1967, the Trombay unit of FCI Ltd. is producing high analysis ammonium phosphate-nitrate fertilizers, commercially known as Suphala, of various grades, viz. 20-20-0, 20-20-20, 15-15-15 (containing 30 per cent of the total P_2O_5 in water-soluble form), from nitric acidulation of phosphate rock. In future also a number of plants for producing complex fertilizers based on nitric acidulation of rock phosphate will be set up in different fertilizer plants of India. It was, therefore, considered desirable to undertake a detailed study of nitric acidulation of rock phosphate. Some workers[1–6] have already studied this reaction in presence of large excess of dilute nitric acid or other conditions which did not correspond to the conditions prevailing in nitrophosphate plants. In the present work, kinetics of the rock phosphate-nitric acid reaction has been studied by simulating conditions prevailing in commercial nitrophosphate plants. Rock phosphate samples obtained from different sources, including those of Indian origin, were reacted with different amounts and concentration of nitric acid at various temperatures. The dependence of the degree of decomposition of the rock phosphates on the nitric acid concentration, temperature and interaction time was studied. From the experimental data, the order of the reaction and the activation energy were calculated.

Experimental

The decomposition of phosphate rock by nitric acid involves various factors, such as (a) intrinsic property and particle size of the phosphate rock, (b) acidulation time, (c) acid concentration and (d) temperature. The experiments performed were planned in such a manner that all the factors given above were taken into consideration.

Rock phosphate from three different sources, viz. Jhamarkotra, Nauru and Jordan (Table 1) ground to pass 200 mesh (BSS) sieve, were reacted under similar conditions in order to observe the differences in their reactivity.

The stock solution of nitric acid used in these investigations was of A.R.B.D.H. quality, from which different concentrations of acids were prepared by dilution, and the chemicals used were also of A.R.B.D.H. quality unless otherwise stated. The P_2O_5 content of the slurry obtained after acidulation was determined by a spectronic-20 spectrocolorimeter by employing the colorimetric phosphovanadomolybdate method. The results of colorometric determinations of P_2O_5 were also confirmed by the standard gravimetric method in many cases.

TABLE 1—CHEMICAL ANALYSIS OF DIFFERENT ROCK PHOSPHATE SAMPLES

Nos.	Ingredients	Rock Phosphates, w/w %		
		Jhamarkotra	Nauru	Jordan
1.	P_2O_5	37.998	36.087	32.790
2.	CaO	52.162	52.598	52.020
3.	Isolubles & SiO_2	3.870	0.492	2.980
4.	Moisture	0.300	0.721	0.400
5.	SO_3	Traces	3.580	0.450
6.	Mixed Oxide	1.580	0.880	0.950
7.	CO_2	Traces	1.960	4.080
8.	F	3.350	3.080	3.590

The experiments were performed in a three-necked round bottom pyrex glass reactor of one lit. capacity. The reactor was fitted with a stainless steel stirrer, kept at a constant speed, inserted through one of its necks; through the second neck a thermometer was inserted. Through the third neck, the rock was added and the slurry was taken out. Weighed amounts of nitric acid (100 g. in each case) of the desired concentration were put in the reactor, which was then placed in a thermostat set at a temperature at which the reaction was to be carried out. When the acid attained the temperature of the thermostat, weighed amount of phosphate rock (50 g. in each case) was added to it slowly, with constant stirring. The slurry, thus prepared, was taken out at different intervals and immediately quenched in ice to stop the reaction. The initial time of the reaction was taken to be the moment when addition of rock to the acid had just completed.

It was observed that in the experiments with each rock phosphate sample the reaction was very fast and vigorous in the beginning, so it was not possible to take out slurry samples for analysis immediately after the addition of rock to acid was completed. The time elapsed before first samples of slurry were taken out for analysis were different for different rocks depending upon their constituents; thus, in case of Jhamarkotra and Nauru rocks only 2.5 min. were required whereas in case of Jordan rock it was 5 min. (in this case there was too much frothing and effervescence). The slurries, thus taken out at different intervals of time, were frozen in ice and were analysed for their soluble P_2O_5 contents; kinetics of reaction was studied from the data obtained. Studies were made with each rock by varying the following conditions. (i) the reaction time from 2.5 to 90 min.; (ii) temperature from 30 to 70°C; and (iii) the acid concentration from 30 to 90 per cent (Tables 2-7).

Results and Discussion

When rock phosphate is treated with nitric acid, reactions take place according to the equations given below, depending upon the amounts and concentrations of the acid.

$$3Ca_3(PO_4)_2CaF_2 + 20HNO_3 \rightarrow 6H_3PO_4 + 10\,Ca(NO_3)_2 + 2HF \quad (1)$$

$$3Ca_3(PO_4)_2CaF_2 + 18HNO_3 \rightarrow 4H_3PO_4 + Ca(H_2PO_4)_2 + 9Ca(NO_3)_2 + 2HF \quad (2)$$

$$3Ca_3(PO_4)_2CaF_2 + 14HNO_3 \rightarrow 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 2HF \quad (3)$$

It can be seen from the above equations that when nitric acid is added to the rock phosphate, the insoluble P_2O_5 present in the rock becomes soluble in different forms depending upon the amount of the acid present. When the nitric acid is present in excess, the P_2O_5 becomes soluble as phosphoric acid (equation 1); when the amount of nitric acid in the system is less than that in (1), the P_2O_5 becomes soluble as a mixture of monocalcium phosphate and phosphoric acid the amount of which is still less.

To study these and other aspects of rock phosphate-nitric acid reaction, the above three rock phosphates were reacted with different concentrations of nitric acid (30 to 90 per cent) at different temperatures (30° to 70°C)

TABLE 2—DECOMPOSITION OF JHAMARKOTRA ROCK PHOSPHATE AT 50°C ± 1 WITH NITRIC ACID (BDH)
[Time of addition of rock to the acid = 20 sec.]

[50 g. rock phosphate and 100 g. nitric acid of different concentrations were taken for each experiment.]

Nos.	CaO/HNO_3 Ratio in the Rock	Concentration of HNO_3, w/w %	% P_2O_5 Decomposed					
			2.5 min.	5 min.	10 min.	20 min.	40 min.	60 min.
1.	1:1.15	30.0	72.86	73.67	74.01	76.35	82.33	83.29
2.	1:1.53	40.0	74.82	83.98	86.75	78.60	92.66	93.96
3.	1:1.91	50.0	85.21	89.25	91.13	92.23	94.29	95.72
4.	1:2.01	52.50	85.32	89.33	91.60	93.31	95.28	96.38
5.	1:2.11	55.0	85.44	89.80	92.02	93.32	96.16	97.27
6.	1:2.20	57.50	85.54	90.03	93.02	94.44	96.40	97.65
7.	1:2.30	60.0	86.17	91.83	94.55	96.60	98.56	99.19
8.	1:2.39	62.50	84.48	89.69	93.23	95.23	97.72	98.87
9.	1:2.49	65.0	85.29	89.31	93.02	94.04	94.92	95.83
10.	1:2.59	67.50	85.38	89.08	91.01	92.51	93.97	94.92
11.	1:2.68	70.0	85.92	88.65	89.18	90.44	92.04	94.14
12.	1:3.06	80.0	84.97	86.51	87.88	88.77	90.82	92.23
13.	1:3.45	90.0	84.08	86.13	87.57	88.02	90.39	92.04

TABLE 3—DECOMPOSITION OF NAURU ROCK PHOSPHATE AT 50°C ± 1 WITH NITRIC ACID (BDH)
[Time of rock addition to acid = 18 sec.]

[50 g. Rock Phosphate and 100 g. Nitric Acid of different concentrations were taken for each experiment.]

Nos.	CaO/HNO_3 Ratio in the Rock Acidulation	Concentration of HNO_3, w/w %	% P_2O_5 Decomposed					
			2.5 min.	5 min.	10 min.	20 min.	40 min.	60 min.
1.	1:1.14	30.0	79.14	80.48	82.26	83.46	86.02	87.35
2.	1:1.52	40.0	85.01	86.98	88.95	90.23	93.03	94.78
3.	1:1.61	42.50	85.60	87.25	89.39	91.67	94.01	95.94
4.	1:1.71	45.0	86.25	88.02	90.11	91.93	94.16	96.02
5.	1:1.80	47.50	86.35	88.34	90.80	92.34	94.60	96.51
6.	1:1.90	50.0	87.34	91.35	92.91	95.18	97.16	98.02
7.	1:1.99	52.50	88.34	91.95	93.28	96.67	97.62	98.62
8.	1:2.09	55.0	88.85	92.27	94.55	97.27	98.74	99.02
9.	1:2.18	57.50	88.24	90.65	94.05	95.47	97.11	98.78
10.	1:2.28	60.0	87.78	89.38	93.27	94.12	96.43	98.12
11.	1:2.66	70.0	87.04	88.95	93.05	93.90	95.85	97.92
12.	1:3.04	80.0	86.87	87.78	92.80	93.30	94.70	97.13
13.	1:3.42	90.0	86.12	87.34	90.95	92.90	93.85	96.45

TABLE 4—DECOMPOSITION OF JORDAN ROCK PHOSPHATE AT 50°C ± 1 WITH NITRIC ACID (BDH)
[Time of rock addition to acid = 30 sec.]

[50 g. Rock Phosphate and 100 g. Nitric Acid of different concentrations were taken for each experiment.]

Nos.	CaO/HNO_3 Ratio in the Rock Acidulation	Concentration of HNO_3, w/w %	% P_2O_5 Decomposed					
			2.5 min.	10 min.	20 min.	40 min.	60 min.	90 min.
1.	1:1.11	30.0	67.40	67.68	68.32	71.69	80.33	86.07
2.	1:1.53	40.0	71.84	73.87	74.01	78.88	83.77	87.86
3.	1:1.92	50.0	73.87	74.73	76.20	79.92	84.78	89.14
4.	1:2.02	52.5	74.35	75.04	76.93	80.59	85.31	89.80
5.	1:2.11	55.0	75.04	75.71	77.55	81.37	86.02	89.86
6.	1:2.21	57.5	75.11	76.56	78.52	81.75	86.19	91.28
7.	1:2.30	60.0	75.16	76.14	78.95	81.80	86.21	92.21
8.	1:2.40	62.5	75.23	75.96	79.08	83.09	86.93	92.66
9.	1:2.49	65.0	75.16	76.14	78.95	81.45	86.69	90.11
10.	1:2.59	67.5	73.92	74.60	78.39	80.59	83.29	87.11
11.	1:2.69	70.0	71.77	76.56	77.98	80.53	81.86	84.33
12.	1:3.07	80.0	71.20	73.38	77.12	78.83	80.53	83.46
13.	1:3.46	90.0	70.89	73.26	76.20	77.98	80.02	82.43

TABLE 5—DECOMPOSITION OF JHAMARKOTRA ROCK PHOSPHATE WITH NITRIC ACID (BDH) AT DIFFERENT TEMPERATURES
[Time of rock addition to acid = 20 sec.]

[50 g. Rock Phosphate and 100 g. Nitric Acid of optimum concentration were taken for each temperature.]

a = % of total P_2O_5 per 100 g. of slurry.
x = % of soluble P_2O_5 per 100 g. of slurry in a particular time.
k = velocity constant.

Nos.	Temp., °K ± 1	Concentration of HNO_3, w/w %	Soluble P_2O_5 in 100 g. of Slurry						$\frac{k}{1 \times 10^{-4}}$
			2.5 min.	5 min.	10 min.	20 min.	40 min.	60 min.	
1.	303	60.0	10.495	10.944	11.496	11.558	11.814	11.913	6.165
2.	313	60.0	10.888	11.613	11.948	12.276	12.408	12.490	6.338
3.	323	60.0	10.801	11.622	11.961	12.330	12.460	12.552	7.030
4.	333	60.0	10.911	11.172	11.492	11.967	12.124	12.462	8.810
5.	343	60.0	10.810	11.035	11.264	11.866	12.050	12.284	9.268

TABLE 6—DECOMPOSITION OF NAURU ROCK PHOSPHATE WITH NITRIC ACID (BDH) AT DIFFERENT TEMPERATURES
[Time of rock addition to acid = 18 sec.]

[50 g. of Rock Phosphate and 100 g. Nitric Acid of optimum concentration were taken for each temperature.]

a = % of total P_2O_5 per 100 g. slurry.
x = % of solution P_2O_5 per 100 g. slurry in a particular time.
k = velocity constant.

Nos.	Temp , °K ±. 1	Concentration of HNO_3, w/w %	Soluble P_2O_5 in 100 g. of Slurry						$\frac{k}{1 \times 10^{-4}}$
			2.5 min.	5 min.	10 min.	20 min.	40 min.	60 min.	
1.	303	55.0	10.531	10.842	11.234	11.416	11.858	11.981	7.328
2.	313	55.0	10.709	11.104	11.380	11.640	11.854	12.080	8.128
3.	323	55.0	11.123	11.343	11.581	11.703	11.981	12.097	9.120
4.	333	55.0	11.187	11.273	11.338	11.571	11.738	11.973	11.614
5.	343	55.0	11.091	11.128	11.233	11.451	11.684	11.890	12.882

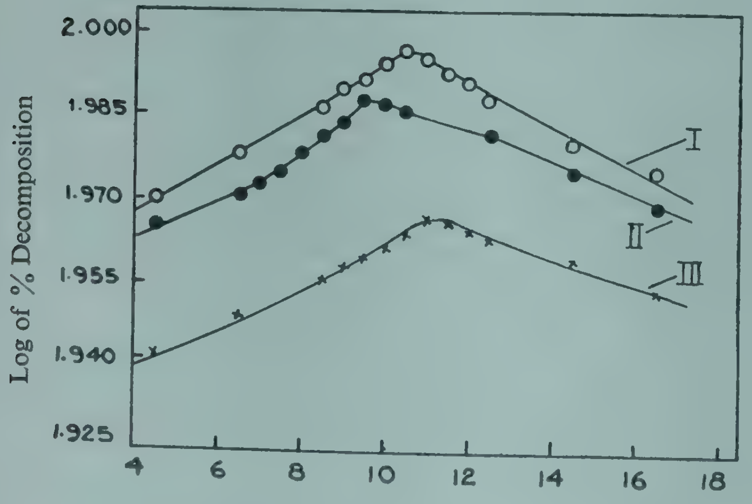
TABLE 7—DECOMPOSITION OF JORDAN ROCK PHOSPHATE WITH NITRIC ACID (BDH) AT DIFFERENT TEMPERATURES
[Time of rock addition to acid = 30 sec.]

[50 g. of Rock Phosphate and 100 g. Nitric Acid of optimum concentration were taken for each temperature.]

a = % of total P_2O_5 per 100 g. slurry.
x = % of soluble P_2O_5 per 100 g. slurry in a particular time.
k = velocity constant.

Nos.	Temp., °K ± 1	Concentration of HN_3O, w/w %	Soluble P_2O_5 in 100 g. of Slurry						$\frac{k}{1 \times 10^{-4}}$
			5 min.	10 min.	20 min.	40 min.	60 min.	90 min.	
1.	303	62.50	7.805	8.004	8.118	8.415	8.602	8.817	4.168
2.	313	62.50	8.00	8.110	8.405	8.614	8.827	9.286	6.025
3.	323	62.50	8.208	8.330	8.638	8.958	9.500	10.108	6.471
4.	333	62.50	8.316	8.528	8.814	9.263	9.671	9.915	7.014
5.	343	62.50	8.421	8.610	8.820	9.314	9.586	9.853	8.974

(Tables 2-4 & Fig. 1). It will be observed that at a definite temperature, there is a particular concentration of nitric acid at which the solubilization of rock phosphate is maximum. In Fig. 1 logarithm of per cent decomposition against nitric acid concentration has been plotted for each rock phosphate and each curve shows a maximum corresponding to a particular acid concentration. Thus at 50°C, maximum solubilization with nitric acid is attained for Jhamarkotra, Nauru and Jordan rock phosphates at 60, 55 and 62.5 per cent acid respectively. The degree of solubilization at these optimum acid concentrations, however, is only slightly greater than that with the lowest concentration, i.e. 30 per cent, of the nitric acid used. This confirms that the P_2O_5 is becoming available in different forms with the least and maximum amounts of acids taken (equations 1, 2 and 3).



HNO$_3$ Conc., g. eqv/l. × 10^{-1}
Fig. 1—Logarithm of Per-cent Decomposition Against Nitric Acid Concentration.
I—Jhamarkotra Rock-Phosphate
II—Nauru Rock Phosphate
III—Jordan Rock Phosphate

It will also be observed from the results (Tables 2-4) that at the initial stage the reaction between rock phosphate and nitric acid is quite fast so that a substantial portion of the rock is solubilized within a short interval of time. Thus, 73 to 86 per cent of P_2O_5 in Jhamarkotra rock and 77 to 88 per cent of P_2O_5 in Nauru rock go into solution 2.5 min. after completion of rock addition while in case of Jordan sample 67 to 75 per cent of P_2O_5 in the rock is solubilized 5 min. after completion of rock addition.

For studying the kinetics of the reaction between rock phosphate and nitric acid, the optimum concentrations of nitric acid which gives the maximum decomposition were first determined for each rock and with this concentration of acid the detailed study was performed. If 'a' is the initial concentration of P_2O_5 in the rock, i.e. the maximum amount of P_2O_5 solubilized after 60 to 90 min. when no further increase in soluble P_2O_5 in the slurry is observed and x is the amount of P_2O_5 solubilized at time t, the amount of P_2O_5 remaining insoluble will be a−x. Hence, for a first order reaction

$$K = \frac{2.303}{t} \text{Log} \frac{a}{a-x} \qquad (4)$$

In the Tables 5, 6 and 7 are given the values of a and x for different rocks at definite temperatures. The experiments performed with all the three rocks show that the plot of time t against log $\frac{a}{a-x}$ gives a straight line (Fig. 2); this proves that the reaction in all the three cases are of first order. Earlier, some authors,[1,6,3] who performed rock-nitric acid reaction under different conditions, have also obtained first order relationships. The slope of these curves (Fig. 2) gives the value of K, the rate constant of

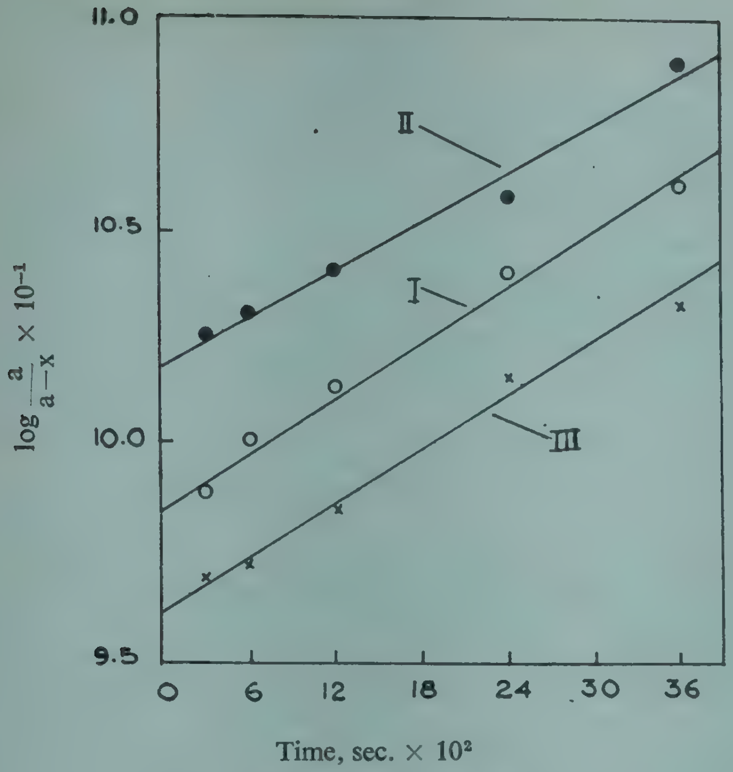


Fig. 2—Plot of Time against log a/a–x.
I—Jhamarkotra Rock Phosphate
II—Nauru Rock Phosphate
III—Jordan Rock Phosphate

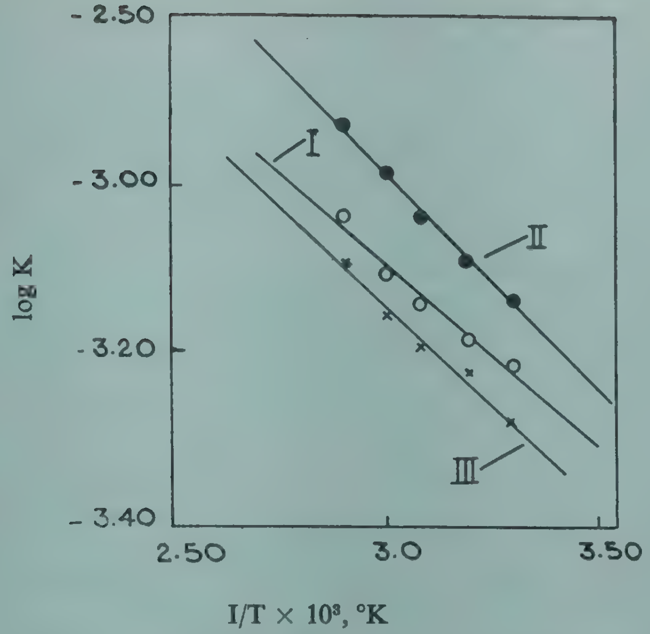


Fig. 3—Logarithm of Rate Constant against Absolute Temperature.
I—Jhamarkotra Rock Phosphate
II—Nauru Rock Phosphate
III—Jordan Rock Phosphate

reactions. The reaction rate constant with Jordan rock and hence its reactivity is less than that with Nauru and Jhamarkotra rocks.

The effects of temperature on the rate of reaction between different rock phosphates and nitric acid have also been studied. According to Arrhenius, the effect of temperature on a chemical reaction can be expressed as

$$K = Ae^{-E/RT} \tag{5}$$

where R is the gas constant, K the rate constant, T the absolute temperature and A and E are the constants related to the particular reaction, E is called the energy of activation, upon taking log of the above equation.

$$\text{Log K} = \text{Log A} - \frac{E}{2.303RT} \tag{6}$$

Hence the graph plotted between log K and $\frac{I}{T}$ will be linear and the slope of this line will be equal to $\frac{E}{2.303RT}$ from which the energy of activation of the reaction can be calculated. Experiments were performed at different temperatures with optimum concentrations of nitric acid in case of each rock and the readings were taken at different intervals of time. The rate constants at different temperatures were then calculated (Fig. 2 and Tables 5, 6 and 7). These values of rate constants at different temperatures were then utilized for determining the activation energy by plotting log K against $\frac{I}{T}$. In each case, a straight line is obtained (Fig. 3), which proves that the reaction between rock phosphate and nitric acid obeys the Arrhenius equations. The energy of activation with Jhamarkotra, Nauru and Jordan rocks were found to be 5.122, 5.671 and 4.085 KCal/mole respectively.

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[Original Mss. received on Jan. 26, 1973]

UDC 633.11: 631 – 82: 631.4 (541.4)

A study of crop responses to nitrogen, phosphorus and potassium on the high-yielding wheat (S-308) was undertaken in Bihar during 1969-70 in the cultivators' fields scattered over 16 districts. Responses to nitrogen, phosphorus and potassium had varying effects in the different agroclimatic regions. The effect of nitrogen at both the 60 and 120 kg./ha levels and phosphorus (22.0 and 44.0 kg.P/ha) in the presence of nitrogen, in general, showed positive responses and were significantly higher than the lower levels. Regarding potash (42.0 and 84.0 kg. K/ha), the responses were divergent and in most of the cases positive, except in the case of the young alluvium soil where it had a depressing effect on the yield. The correlation between per cent yield and soil test values were significant for pH, organic carbon and available phosphorus. The study may be useful in predicting fertilizer doses to cultivators' fields for obtaining optimum yields.

Response of High-Yielding Wheat (S-308) to Nitrogen Phosphate and Potash in Soils of Bihar

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Introduction

Judicious and economic use of fertilizers by the cultivators plays an important part in increasing crop production, thus making the Green Revolution a success. For economic use of fertilizers, simple fertilizer trials in the cultivators' fields were first started in Bihar in 1948[1,2]. During 1953-56 six types of experiments were introduced wherein nitrogen, phosphorus and potassium were tried each at two dose levels[3]. Nitrogen was tried alone and in combination with phosphorus and potassium. In 1956, 3 × 3 × 3 trials were introduced in the cultivators' fields with nitrogen, phosphorus and potassium, in which higher order interactions were partially confounded with blocks[4]. The method of statistical analysis of such trials has been introduced earlier[3].

Due to the heterogenety in soils of Bihar and also the introduction of new high-yielding varieties of wheat, it was found necessary by the Fertilizer Promotion and Agricultural Research Centre of this Division to undertake fertilizer trials in the cultivators' fields. The agronomical studies on relative efficiencies of citrate- and water-soluble, straight and complex phosphates as well as straight nitrogenous fertilizers were undertaken[6].

The present study was undertaken: (i) to demonstrate to the farmers the additional yield and thereby higher profits that can be obtained in their own fields by using fertilizers and improved seed; (ii) to study the magnitude of response of high-yielding wheat to nitrogen, phosphorus and potassium under different agro-climatic zones; and (iii) to formulate fertilizer schedules for each block, district and soil type.

Experimental Methods

The experiments were conducted on cultivators' fields in 43 selected community development blocks involving 16 districts of Bihar. These districts and the blocks within the districts represent four major types of soils, viz. old alluvium, young alluvium, recent alluvium and red loam or sedentary soils. There were seven treatments, viz. Control, N_1, N_2, N_2P_1, N_2P_2, $N_2P_1K_1$ and $N_2P_2K_2$, where N_1 and N_2 represent 60 and 120 kg./ha of nitrogen in the form of urea, P_1 and P_2 as 22.0 and 44.0 kg./ha of phosphorus in the form of single superphosphate and K_1 and K_2 as 42.0 and 84.0 kg.K/ha in the form of muriate of potash. The plot size was 50 sq.m. and each experiment with 3 replications was placed at one site in a village with irrigation facilities in the selected blocks*.

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*Political division of a district normally including about one hundred villages.

These experiments were conducted in randomized block design.

The response for nitrogen was taken as absolute, for phosphate as response over N_2 and the response for K_1 was taken over N_2P_1 and for K_2 over N_2P_2 treatment.

The data on the yield of grain and straw was noted and the analysis of variance was done by the usual method. The percentage yield and per cent yield response were calculated as follows:

$$\% \text{ yield} = \frac{y_o}{y_i} \times 100$$

$$\% \text{ yield response} = \frac{y_i - y_o}{y_i} \times 100,$$

where y_o = yield without nutrient, and y_i = yield with adequate nutrient application.

The per cent yield values at N_2 and P_2 were correlated with soil test values of pH, organic carbon and available phosphorus. The means of soil test values of pH, electrical conductivity, organic carbon and available phosphate are presented in Table 1.

The results of the response of wheat to the application of nitrogen, phosphorus and potassium are presented in Tables 2, 3 and 4 respectively. The yield values presented (Tables 2-4) are absolute for control, while those under the treatments of nitrogen, phosphorus and potassium are increase over control or the respective lower levels.

The per cent yield responses of wheat to the application of nitrogen, phosphorus and potassium as calculated above was classified into the following: those less than 20 per cent as low, between 20 and 50 per cent as medium and those higher than 50 per cent as high. The results are presented in Table 5.

Results and Discussion

Old Alluvium

This soil type includes the area between the south bank of Ganges and Chhotanagpur region covering Patna, Gaya, Sahabad and Bhagalpur districts. In general, the soil is heavy in texture and neutral in reaction. The total

TABLE 1—MEAN VALUES OF pH, ELECTRICAL CONDUCTIVITY, ORGANIC MATTER AND AVAILABLE PHOSPHORUS CONTENT OF THE SOILS

District	No. of Composite Soil Samples Tested for each trial	pH	EC mmho./cm.	Organic Matter, %	Available P, kg./ha
Patna	6	7.1	0.17	0.50	10.0
Gaya	6	7.1	0.10	0.61	28.8
Sahabad	6	7.4	0.18	0.67	22.6
Bhagalpur	2	7.4	0.77	1.44	45.7
Old alluvium	20	7.2	0.21	0.67	23.0
Muzzaffarpur	3	8.6	0.33	0.93	18.0
Darbhanga	4	9.0	0.57	0.85	4.4
Saran	4	7.8	0.32	1.28	54.0
Monghyr (N)	3	8.2	0.45	0.97	16.8
Young alluvium	14	8.4	0.42	1.02	24.1
Purnea	4	7.1	0.13	0.78	26.4
Saharsa	7	8.3	0.20	0.66	6.7
Recent alluvium	11	7.9	0.19	0.71	10.4
S. Parganas	6	6.4	0.09	0.93	6.6
Ranchi	5	7.3	0.38	1.26	19.9
Palamau	6	7.5	0.25	1.04	6.4
Hazaribagh	2	7.0	0.13	1.04	8.7
Singhbhum	5	6.5	0.15	1.23	13.0
Dhanbad	1	6.0	0.05	0.47	13.1
Red loam (Sedentary)	25	6.4	0.20	1.07	10.9

TABLE 2—Response of Wheat (S-308) to the Application of Nitrogen in Soils of Bihar

District	No. of Trials	Grain Yield, q./ha				Straw Yield, q./ha			
		Control	60 kg N/ha	120 kg N/ha	SE ±	Control	60 kg N/ha	120 kg N/ha	SE ±
Patna	6	11.88	4.04	5.19	1.25	15.01	4.36	5.92	1.43
Gaya	6	13.28	9.67	12.59	1.90	19.93	14.47	18.81	2.93
Sahabad	6	17.55	10.99	19.44	3.59	22.28	14.15	26.04	1.82
Bhagalpur	2	13.23	2.57	10.18	1.39	16.37	3.83	12.88	2.31
Old alluvium	20	14.13	7.66	12.18	2.24	18.80	10.27	16.51	2.19
Muzaffarpur	3	17.22	9.00	13.00	0.91	27.78	12.89	21.55	1.62
Darbhanga	4	27.08	2.97	7.04	1.90	34.45	3.62	9.03	2.42
Saran	4	15.00	4.83	8.83	0.73	23.50	6.67	11.83	1.49
Monghyr (N)	3	17.33	10.21	9.94	0.75	—	—	—	—
Young alluvium	14	19.42	6.34	9.45	1.17	28.65	7.26	13.46	1.89
Purnea	4	13.29	6.67	9.79	2.43	32.46	9.75	16.83	5.44
Saharsa	7	8.47	1.47	2.41	2.06	—	—	—	—
Recent alluvium	11	10.22	3.36	5.09	2.25	32.46	9.75	16.83	5.44
S. Parganas	6	18.78	4.00	7.44	2.15	37.55	8.01	14.89	4.29
Ranchi	5	17.48	9.48	12.76	1.21	36.98	17.62	33.41	2.98
Palamau	6	17.44	7.24	20.89	0.81	—	—	—	—
Hazaribagh	2	13.16	2.50	1.69	2.87	30.66	6.34	0.34	6.73
Singhbhum	5	7.33	2.79	6.21	1.10	12.89	4.31	8.78	1.47
Dhanbad	1	8.17	3.23	4.93	0.11	11.17	5.66	8.76	0.46
Red loam (Sedentary)	25	15.03	5.48	10.92	1.64	28.80	9.27	16.30	3.87
Mean for Bihar state	70	14.90	5.95	10.00	1.80	25.33	9.27	15.84	3.23

TABLE 3—Response of Wheat (S-308) to the Application of Phosphate in Soils of Bihar

District	No. of Trials	Grain Yield, q./ha			Straw Yield, q./ha		
		22.0 kg P/ha	44.0 kg P/ha	SE ±	22.0 kg P/ha	44.0 kg P/ha	SE ±
Patna	6	8.06	16.86	1.25	8.44	18.23	1.43
Gaya	6	5.53	5.47	1.90	9.03	8.27	2.93
Sahabad	6	9.99	17.62	3.59	11.77	20.21	1.82
Bhagalpur	2	4.02	7.49	1.39	0.32	3.68	2.31
Old alluvium	20	7.48	12.73	2.24	8.80	14.38	2.19
Muzaffarpur	3	9.95	12.13	0.91	15.22	16.00	1.62
Darbhanga	4	4.94	11.11	1.90	6.02	13.84	2.42
Saran	4	1.84	3.83	0.73	1.67	2.00	1.49
Monghyr (N)	3	13.50	18.24	0.75	—	—	—
Young alluvium	14	6.96	10.78	1.17	6.95	10.12	1.89

Continued)

TABLE 3 (*Contd.*)—Response of Wheat (S-308) to the Application of Phosphate in Soils of Bihar

District	No. of Trials	Grain Yield, q./ha			Straw Yield, q./ha		
		22.0 kg P/ha	44.0 kg P/ha	SE ±	22.0 kg P/ha	44.0 kg P/ha	SE ±
Purnea	4	13.29	18.63	2.43	24.33	33.46	5.44
Saharsa	7	3.74	6.08	2.06	—	—	—
Recent alluvium	11	7.21	10.64	2.25	24.33	33.46	5.44
S. Parganas	6	3.06	7.89	2.15	6.12	15.78	4.29
Ranchi	5	4.16	7.84	1.21	3.94	7.60	2.98
Palamau	6	1.57	0.17	0.81	—	—	—
Hazaribagh	2	1.50	9.83	2.87	−2.00	23.66	6.73
Singhbhum	5	5.68	10.55	1.10	9.10	17.50	1.47
Dhanbad	1	1.37	1.70	0.11	1.27	1.34	0.46
Red loam (Sedentary)	25	3.48	6.47	1.64	5.22	14.15	3.87
Mean for Bihar State	70	5.74	9.78	1.80	6.41	14.84	3.23

TABLE 4—Response of Wheat (S-308) to the Application of Potash in Soils of Bihar

District	No. of Trials	Grain Yield, q./ha			Straw Yield, q./ha		
		42.0 kg K/ha	84.0 kg K/ha	SE ±	42.0 kg K/ha	84.0 kg K/ha	SE ±
Patna	6	8.06	3.11	1.25	8.51	2.45	1.43
Gaya	6	−0.49	0.90	1.90	−1.40	1.26	2.93
Sahabad	6	1.10	1.80	3.59	1.58	2.19	1.82
Bhagalpur	2	8.35	3.38	1.39	8.93	4.12	2.31
Old alluvium	20	3.44	2.08	2.24	3.50	2.18	2.19
Muzaffarpur	3	−7.89	−6.78	0.91	−13.10	−11.00	1.62
Darbhanga	4	−13.54	−12.22	1.90	16.62	15.40	2.42
Saran	4	4.16	6.92	0.73	5.16	8.50	1.49
Monghyr (N)	3	−11.40	−12.44	0.75	—	—	—
Young alluvium	14	−6.81	−5.63	1.17	4.35	4.92	1.89
Purnea	4	9.38	−2.18	2.43	19.14	−0.95	5.44
Saharsa	7	8.70	10.30	2.06	—	—	—
Recent alluvium	11	8.95	5.76	2.25	19.14	−0.95	5.44
S. Parganas	6	4.61	1.17	2.15	9.22	2.34	4.29
Ranchi	5	6.52	7.28	1.21	7.11	10.39	2.98
Palamau	6	−1.00	6.48	0.81	—	—	—
Hazaribagh	2	6.33	−3.00	2.87	13.00	−8.33	6.73
Singhbhum	5	5.12	9.03	1.10	9.84	14.80	1.47
Dhanbad	1	−0.44	1.37	0.11	−0.57	1.93	0.46
Red loam (Sedentary)	25	3.68	4.91	1.64	8.71	6.35	3.87
Mean for Bihar State	70	2.34	2.13	1.80	6.66	4.22	3.23

TABLE 5—CLASSIFICATION OF THE RESPONSE OF WHEAT (S-308) TO N, P, K APPLICATION IN SOILS OF DIFFERENT BLOCKS

Soil Type	Classification	% Response to 60 kg. N/ha	% Response to 120 kg N/ha	No. of Blocks	% Response to 22.0 kg. P/ha	% Response to 44.0 kg. P/ha	No. of Blocks	% Response to 42.0 kg. K/ha	% Response to 84.0 kg. K/ha	No. of Blocks
Old Alluvium	Low	−6.7	2.0	1	6.1	7.3	6	1.8	4.6	15
	Medium	25.2	34.2	9	23.8	35.2	10	30.4	7.4	5
	High	46.2	56.2	10	46.2	59.8	4	—	—	—
Young Alluvium	Low	0.9	5.3	2	7.6	14.9	6	−12.2	−9.1	10
	Medium	29.1	38.3	12	26.1	33.9	8	25.7	20.8	4
	High	—	—	—	—	—	—	—	—	—
Recent Alluvium	Low	10.5	12.9	5	−8.2	11.2	2	11.0	1.9	2
	Medium	21.6	38.6	5	23.3	38.9	6	23.8	16.8	6
	High	43.7	50.3	1	40.4	54.8	3	60.3	44.5	3
Red loam (Sedentary)	Low	10.2	9.4	4	6.2	6.0	11	4.1	11.0	16
	Medium	22.6	38.4	13	13.4	32.7	12	27.0	13.9	9
	High	41.9	58.6	8	32.0	54.1	2	—	—	—

soluble salts are normal, organic matter content low and available phosphate medium to high.

The average response to nitrogen at 60 kg. nitrogen level was about 7.7 q./ha. and an additional response over the first level was about 4.5 q./ha. at 120 kg. nitrogen level. Among the districts within this soil, Sahabad at both the levels showed the highest response while it was low in Patna and was the lowest in Bhagalpur district at 60 kg. nitrogen level.

The average response to phosphorus at 22.0 kg./ha. was about 7.5 q/ha while at 44.0 kg/ha it was significantly higher by about 5.2 q/ha than the lower level. The highest response among the districts was again in Sahabad, slightly lower in Patna and was the lowest in Gaya at both the levels.

The response to 120 kg. nitrogen was significantly higher in Sahabad and Bhagalpur districts while at 44.0 kg.P/ha the same was significantly higher in Patna and Bhagalpur districts over the lower levels.

The average response to potash was about 1.4 q/ha more at 42.0 kg.K/ha level than at 84.0 kg,K/ha level. Bhagalpur and Patna districts gave significantly higher response of potash at the lower level. The response of potash in Sahabad and Gaya districts was very low at both the levels.

The responses to nitrogen, phosphorus and potassium in the 20 blocks within the districts representing old alluvium soil (Table 5) were as follows:

% Response	*Area*
Nitrogen	
Low	Phulwari sarif (Patna).
Medium	Bihar sarif (Patna), Bodh Gaya, Sherghati (Gaya); Udwantnagar (Sahabad); Amarpur, Banka (Bhagalpur).
High	Harnaut, Rahui (Patna); Bela (Gaya); Sahapur, Sandesh, Piro (Sahabad).
Phosphorus	
Low	Harnaut (Patna); Bodh Gaya, Bela, Sherghati (Gaya); Amarpur (Bhagalpur)
Medium	Bihar sarif, Phulwari sarif (Patna); Udwantnagar, Sahapur, Sandesh, Piro (Sahabad); Banka (Bhagalpur).
High	Rahui (Patna)
Potassium	
Low	Harnaut, Rahui (Patna); Bodh Gaya, Bela, Sherghati (Gaya); Udwantnagar, Sahapur, Sandesh, Piro (Sahabad); Banka (Bhagalpur).
Medium	Bihar sarif, Phulwari sarif (Patna); Amarpur (Bhagalpur).

Young Alluvium

This area is north of Ganges and includes Muzaffarpur, Darbhanga, Saran, Champaran and North Monghyr districts. The major part of the soil is calcareous with high calcium carbonate (40-45 per cent), high to medium in texture, alkaline in reaction, normal in total soluble salts, medium in organic matter content and medium to high in available phosphate.

The average response to nitrogen and phosphate at 120 kg. nitrogen and 44.0 kg. phosphorus was significantly higher by about 3.1 and 3.8 q/ha respectively over the lower levels. Among the districts representing this soil the highest (13.0 q/ha) response due to 120 kg. nitrogen was obtained in Muzaffarpur and the lowest (7.04 q/ha) in Darbhanga. The highest response of phosphate was obtained in North Monghyr and the lowest in Saran district at both the levels.

In general, 120 kg.N/ha and 44.0 kg.P/ha treatments gave significantly higher response in all the districts studied over the lower levels.

The average response to potash for the soil group as well as the response in the districts representing it has a depressing effect both at 42.0 and 84.0 kg. levels, except in Saran district where a positively significant response to potash was obtained.

Among the blocks within the districts representing this area the response to nitrogen, phosphorus and potassium was as follows:

% Response	*Area*
Nitrogen	
Low	Kalyanpur (Darbhanga)
Medium	Muraul, Sakra I, Mushari (Muzaffarpur); Garkha, Jalapur, Baniapur, Marhawrah (Saran); Pusa, Samastipur (Darbhanga).
High	Begusarai (Monghyr).
Phosphorus	
Low	Garkha, Jalalpur, Baniapur, Marhawrah (Saran); Samastipur, Kalyanpur (Darbhanga).
Medium	Muraul, Sakra I, Mushari (Muzaffarpur), Pusa (Darbhanga); Begusarai (Monghyr).
Potassium	
Low	Muraul, Sakra I, Mushari (Muzaffarpur); Garkha, Jalalpur, Baniapur, Marhawrah (Saran); Begusarai (Monghyr).
Medium	Samastipur, Kalyanpur, Pusa (Darbhanga).

Recent Alluvium

This area comprises the recently deposited soil by the Kosi river and its tributaries. It includes Purnea and Saharsa districts. pH is neutral, total soluble salts normal and organic matter and available phosphate are low.

The average response to 120 kg.N/ha and 44.0 kg. P/ha was higher by about 1.7 and 3.4 q/ha respectively over the lower levels, these differences were, however, non-significant. Higher response to nitrogen and phosphorus was noted in Purnea district compared to that in Saharsa district at both the levels. The response in Purnea district to 44.0 kg.P/ha was significantly higher than 22.0 kg.P/ha.

The average response to potash in this area was higher at 42.0 kg. level by about 3.2 q./ha over the higher level. The response to potash in Purnea district was significantly higher at 42.0 kg. level than 84.0 kg. level. The response in Saharsa district was higher at 84.0 kg. level but it was non-significant.

The distribution of response to nitrogen, phosphorus and potassium among the blocks within the districts of this area is given below:

% Response	*Area*
Nitrogen	
Low	Madhepura, Sourbazar (Saharsa).
Medium	Kirtyanandnagar, Kasba, Purnea (E) (Purnea).
Phosphorus	
Low	Sourbazar (Saharsa).
Medium	Kirtyanandnagar, Kasba (Purnea); Madhepura (Saharsa).
High	Purnea (E) (Purnea).
Potassium	
Low	Purnea (E) (Purnea).
Medium	Kirtyanandnagar, Kasba (Purnea) Madhepura, Sourbazar (Saharsa).

Red Loam or Sedentary

This area comprises the southern part of Bihar and includes Santhal Parganas, Palamau, Hazaribagh, Ranchi, Dhanbad and Singhbhum districts. These soils have been developed *in situ* due to weathering. While the upland soils of this region are red-yellow lateritic and acidic in reaction, the low lands are neutral to alkaline. Total soluble salts in this region are normal, organic matter medium and available phosphate low.

In this region, the average responses to 120 kg.

nitrogen and 44.0 kg. phosphorus were higher by about 5.5 and 3.0 q/ha respectively which were significantly higher over the lower levels.

Among the districts within this region response to nitrogen was the highest in Palamau and the lowest in Hazaribagh, particularly at 120 kg. nitrogen level.

The response to phosphorus and potassium was the highest in Singhbhum at both the levels. There was, in general, higher response due to higher levels of nitrogen and phosphate in most of the districts within this region. In Palamau, Singhbhum and Dhanbad districts 84.0 kg. potassium gave significantly higher yield over 42.0 kg. potassium. But in Hazaribagh significantly higher response was obtained at 42.0 kg. potassium level and the response at 84.0 kg. potassium was depressing. The average response of potash in this region was higher by about 1.2 q/ha at 84.0 kg. level than the 42.0 kg. level.

The block-wise distribution of the response to nitrogen, phosphorus and potassium within the districts in this area is as follows:

% Response	*Area*
Nitrogen	
Low	Hazaribagh; Jama (Santhal parganas).
Medium	Gobindpur (Dhanbad); Chaibasa, Chakradharpur (Singhbhum); Kanke, Kuru (Ranchi); Dumka, Raneswar, Kathiakund (Santhal-parganas).
High	Jugasalai (Singhbhum), Nankum (Ranchi); Bishrampur, Patan (Palamau).
Phosphorus	
Low	Gobindpur (Dhanbad); Kanke, Kuru (Ranchi), Bishrampur, Patan (Palamau).
Medium	Chakradharpur, Chaibasa, Jugasalai (Singhbhum); Hazaribagh; Nankum (Ranchi); Jama, Dumka, Kathiakund (Santhal parganas).

% Response	*Area*
Potassium	
Low	Gobindpur (Dhanbad); Chakradharpur (Singhbhum);Kanke, Kuru, Nankum (Ranchi); Bishrampur, Patan (Palamau); Dumka, Jama, Raneswar (Santhalparganas).
Medium	Chaibasa, Jugasalai (Singhbhum); Hazaribagh, Kathiakund (Santhal parganas).

The preceding results show that majority of the trials conducted on the old alluvium, young alluvium, recent alluvium and red-loam soils, in general, gave positive response of high-yielding wheat at both the levels of nitrogen and phosphorus tried, thus indicating that by and large these soils are deficient in nitrogen and available phosphate contents and a good response of nitrogenous and phosphatic fertilizers may be expected. Correlation studies between the initial soil properties and the per cent grain yield show the following relationships:

CORRELATION STUDIES BETWEEN PERCENT GRAIN YIELD AND SOIL TEST VALUES

% Yield (Y) due to	Soil Properties (X)			Regression Equation
	pH	Org. Carbon	Available P	
120 kg N	0.29*	—	—	$\log Y = 1.561 + 0.0289 X$
120 kg N	—	– 0.22	—	$Y = 0.050 - 0.0029 X$
44.0 kg P	0.04	—	0.26*	$\log Y = 1.736 + 0.0734 \log X$

*Significant value at 5% level

In general, the response to potash in the soils studied was positive in old alluvium, recent alluvium and red-loam soils but depressing in the young alluvium soil, thus indicating a lower availability of potassium in the first three soils than in the last one.

Responses to nitrogen and phosphorus for grain yield were proportional to $(1\text{-}10^{-0.000x})$ where x is the nutrient in kg./ha. when $y = y_0 + d(1\text{-}10^{-kx})$ type of response curve was tried. It shows that the responses to nitrogen and phosphorus up to 120.0 and 44.0 kg level respectively were almost linear in nature. In case of potassium the response at 84.0 kg level was lower than that of 42.0 kg level. So the response in this case was proportional to $0.7230x\text{-}0.0005x^2$.

It may be mentioned here that in earlier experiments in Bihar with local wheat varieties, the K value obtained was nearly 0.01 for nitrogen and phosphorus. For potash, the K value generally changed from year to year and was taken as 0.03. Thus, the high yielding wheat variety showed more linear response to nitrogen and phosphorus application than local varieties invariably reported in the earlier studies[3].

Acknowledgements

Thanks are due to Dr. S. K. Ghosh, Chief Agronomist, and Sarbasri B. Nandi and S. K. Varma, Senior Agronomists and their Field Staff for taking pains in conducting the trials and to the soil testing staff of this Division for their help in analysing the soil samples.

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[Original mss. received on March 17, 1973]

UDC 631.415 (541.4): 546.18

Fractionation of inorganic phosphorus which constituted 70-90 per cent of the total phosphorus in 12 acidic soils of Bihar indicated the various components in the following order: reductant soluble-phosphate, iron phosphate, calcium phosphate, aluminium phosphate and occluded aluminium phosphate. Reductant soluble-phosphate constituted about 50 per cent of the total inorganic phosphorus. About 80-90 per cent of the soluble-phosphate (KH_2PO_4) added at the rate of 50 ppm phosphorus is found to get fixed during 30 days with appreciable increase in reductant soluble-phosphate and iron phosphate forms and to a lesser degree in the aluminium phosphate and calcium phosphate forms.

Fixation of Soluble Phosphate in Some Acidic Soils of Bihar

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Inorganic soil phosphate can be fractionated into the following five groups: aluminium phosphate (Al-P), iron phosphate (Fe-P), calcium phosphate (Ca-P), reductant soluble-phosphate (Red-P) and occluded iron and aluminium phosphate[1] (Occ-P). Fractionation of soil phosphorus is important in order to characterize its availabilty and the weathering and extent of soil development[2]. Marked variations exist in the different forms of inorganic phosphate depending on the nature of the soil. Calcium phosphate dominated in soils of high pH, while the soils having lower pH contained higher amounts of aluminium, iron and reductant soluble-phosphate[3,4]. Singh *et al*[5] noted that in some of the soils of Bihar, inorganic phosphate, which constituted about 70 per cent of the total soil phosphate, on fractionation indicated various components as occluded iron phosphate, calcium phosphate, iron phosphate, aluminium phosphate and occluded aluminium phosphate in sedentary soils, and calcium phosphate, occluded iron phosphate, iron phosphate, occluded aluminium phosphate, and aluminium phosphate in alluvial soils. The fixation of added soluble phosphate in acid soils is well-known. The reactions leading to fixation are fairly rapid[6,7]. Kar and Chakravarti[4] reported that 30 to 50 per cent of the added soluble-

TABLE 1—pH, ORGANIC CARBON AND PHOSPHORUS CONTENT OF SOILS

Soils	pH	Organic C, %	Total P, ppm	Organic P, ppm	Inorganic P, ppm	$\frac{\text{Inorg.}}{\text{Total}}$ × 100 P
Tumar	5.9	0.50	600	90	510	85.0
Rata	5.1	0.40	600	95	505	84.1
Gumla	4.9	0.60	650	85	465	71.5
Bishampur	5.6	0.35	600	75	525	87.5
Kolebira	4.9	0.50	500	70	430	86.0
Sherghati	5.2	0.40	550	110	440	80.0
Khunti	5.6	0.45	600	80	520	86.6
Mandar	5.1	0.35	600	90	510	85.0
Bero	5.9	0.60	650	185	475	73.0
Basia	5.1	0.50	600	180	420	70.0
Kanke	5.3	0.55	600	135	465	77.5
Baliapur	5.7	0.40	500	75	425	75.5

TABLE 2—FRACTIONS OF INORGANIC PHOSPHORUS IN SOILS WITH AND WITHOUT ADDED PHOSPHORUS, ppm

Soils		Saloid-P	Al-P	Fe-P	Ca-P	Red-P	Occ. Al-P	Total P Extracted
Tumar	(a)*	2	9	67	17	300	3	398
	(b)*	12	12	80	27	312	4	447
Rata	(a)	2	6	72	25	260	3	368
	(b)	9	10	85	29	278	5	416
Gumla	(a)	3	6	76	21	250	2	358
	(b)	10	10	92	25	265	4	406
Bishampur	(a)	6	8	98	28	300	4	444
	(b)	10	12	114	33	329	2	492
Kolebira	(a)	3	6	65	17	280	6	377
	(b)	13	10	77	27	292	8	427
Sherghati	(a)	2	5	71	18	220	4	320
	(b)	10	11	85	22	234	6	368
Khunti	(a)	3	6	78	21	270	3	381
	(b)	11	11	90	27	285	5	429
Mandar	(a)	3	7	65	19	280	3	377
	(b)	10	12	80	23	295	6	426
Bero	(a)	4	10	71	30	270	3	388
	(b)	13	15	85	34	285	5	435
Basia	(a)	3	7	75	26	280	4	395
	(b)	12	10	86	33	295	7	443
Kanke	(a)	4	8	68	25	240	4	349
	(b)	14	14	80	29	256	2	395
Baliapur	(a)	6	5	75	27	250	4	369
	(b)	10	12	96	29	265	5	407

a = without P, b = with 50 ppm P

TABLE 3—FRACTIONS OF PHOSPHORUS EXPRESSED AS PERCENTAGE TOTAL INORGANIC PHOSPHORUS

Soil	Al-P	Fe-P	Ca-P	Red-P	Occ. Al-P	Insol-P
Tumur	1.72	12.86	3.26	57.60	0.57	23.42
Rata	1.16	13.39	4.65	48.36	0.55	31.06
Gumla	1.29	16.34	4.51	53.75	0.43	23.05
Bishampur	1.52	18.62	5.32	57.00	0.76	15.39
Kolebira	1.39	15.08	3.94	64.96	1.39	12.29
Sherghati	1.13	16.11	4.08	49.94	0.90	27.24
Khunti	1.15	14.97	4.03	51.84	0.57	26.68
Mandar	1.37	12.74	3.72	54.88	0.58	26.06
Bero	2.10	14.91	6.30	56.70	0.63	18.27
Basia	1.66	17.85	6.18	66.64	0.95	16.89
Kanke	1.52	12.92	4.75	45.60	0.76	24.70
Baliapur	1.32	14.79	5.65	55.79	0.82	24.74

TABLE 4—INCREASE IN DIFFERENT FRACTIONS IN PERCENTAGE OF ADDED PHOSPHORUS

Soil	Sal-P	Al-P	Fe-P	Ca-P	Red-P	Occ. Al-P
Tumar	29	6	26	20	24	2
Rata	14	8	26	8	36	4
Gumla	14	8	32	8	30	4
Bishampur	8	8	32	10	42	−4
Kolebira	20	8	24	20	24	4
Sherghati	16	12	28	8	28	4
Khunti	16	10	24	12	30	4
Mandar	14	10	30	8	30	6
Bero	18	10	28	8	26	4
Basia	18	6	22	7	30	6
Kanke	20	12	24	8	32	−4
Baliapur	16	14	26	6	28	2

phosphate was fixed in 3 months in some acid soils with an appreciable increase in aluminium phosphate, iron phosphate and reductant soluble-phosphate and to a lesser degree in occluded aluminium phosphate. The present investigation was undertaken to fractionate the inorganic phosphate and to study the transformation of the added soluble phosphate in some acid soils of Bihar.

Experimental

Twelve soil samples (0-15 cm.) were collected from different places of Bihar, representating the acidic soils of the State. The determination of total phosphate and total inorganic phosphate were made by the method described by Jackson[8]. Inorganic phosphorus was fractionated by the method of Chang and Jackson[1].

KH_2PO_4 solution at the rate of 50 ppm phosphorus was added to 1 g of each soil sample taken in stoppered tube and incubated for a period of 30 days, at the end of which it was fractionated for phosphorus.

Results and Discussion

The results are presented in Tables 1, 2 and 4.

The total phosphorus in soils (Table 1) varied from 500 to 650 ppm, of which inorganic phosphorus fraction ranged from 70 to 88 per cent. About 72 to 94 per cent of the inorganic phosphorus could be extracted in different forms. Unextractable inorganic phosphorus is accounted as insoluble phosphorus.

Aluminium phosphate is found to vary from 5 to 10 ppm, constituting about 1-2 per cent of the total inorganic phosphorus. Iron phosphate varied from 65 to 98 ppm, corresponding to 12 to 18 per cent of the total inorganic phosphorus. Calcium phosphate constituted about 3-6 per cent. Reductant soluble iron phosphate is found to vary from 220 to 300 ppm and when expressed as percentage the variation would be from 45 to 66 per cent. High amounts of iron phosphate and reductant soluble-phosphate in these soils are in agreement with the findings of Fiskell and Spencer[9], who have shown that native phosphorus exists mainly as iron compounds with lesser amounts of aluminium phosphate and calciul phosphate. Occluded aluminium phosphate is found to be low ranging from 2 to 6 ppm.

A critical examination of the Table 3 reveals that the soils are richer in iron phosphate and reductant soluble iron phosphate in comparison to aluminium phosphate.

From Table 4, it can be noted that 80-92 per cent of the added soluble-phosphate is transformed into various insoluble forms. Highest fixation occured in Bishampur (pH 5.6) and lowest in Tumar (pH 5.9), Kolebira (pH 5.1) and Kanke (pH 5.3) soils. It is also noted that iron phosphate and reductant soluble-phosphate increased significantly. Calcium phosphate also increased as a result of phosphate addition, more so in Tumar and Kolebira soils. Though aluminium phosphate constituted only about 1 to 2 per cent of the total inorganic phosphate, 6 to 12 per cent of the added phosphate got fixed in this form.

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[Original Mss. received on April 20, 1973]

UDC 631.415: 546.18+546.72+546.621

To study the availability of iron and aluminium phosphates in acidic reactions, these phosphates were allowed to react with 4 acid soils (pH 4.73 to 5.76) of West Bengal, and OH-resins at pH 4, 5 and 6 through the intermediary of a cellophane membrane. No marked difference is noted between iron and aluminium phosphate in releasing phosphorus, but the effect of pH is clearly indicated, i.e. higher the soil pH greater is the release. Much higher amount of phosphorus is released by the OH-resin-exchange process, more so at higher pH of the medium; the simultaneous increase in pH is more marked at lower pH.

Availability of Iron and Aluminium Phosphates in Acidic Reactions

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Acid soils contain most of their phosphorus as iron and aluminium phosphates of low solubility. The utilization of phosphorus by plants from these phosphates has been studied by a number of workers, and under normally favourable conditions the availability of phosphorus to plants was found to vary between 75 and 100 per cent of that observed with superphosphate[1]. Direct study of phosphorus uptake by plants has often been replaced for the sake of expediency and convenience by the method of analysing extracts of soil for phosphorus and correlating with plant uptake. Some workers reported that phosphorus extracted by OH-resin gives better correlation than the other extractants with phosphorus uptake by plants[2–4]. The present experiment was carried out to study the availability to iron and aluminium phosphates in acidic reactions using hydroxy resin as the extractant.

Experimental

4 soil samples (0-15 cm.) collected from the following agroclimatic regions of West Bengal were used: hilly forest soil of Darjeeling, Gangetic alluvial soil of Karticpur, 24-Parganas, lateritic soils of Chandrakona, Midnapur and Mohammedbazar, Birbhum. The relevant data on some characteristics of the soils are presented in Table 1.

Iron and aluminium phosphates used were prepared as given below.

Iron Phosphate: Ferric hydroxide was prepared from ferric cholride washed salt-free and suspended in water. Ammonium phosphate was then added and the suspension adjusted to pH 2.5 by the addition of phosphoric acid. The resultant product was washed with water till phos-

TABLE 1—Some Characteristics of the Soils

Soil	Sand, %	Silt, %	Clay, %	Org. C., %	pH	CEC, me/100 g.	Water-Soluble Phosphorus, ppm	HCl-Soluble, %			Total P_2O_5, %
								Fe_2O_3	Al_2O_3	CaO	
Darjeeling	69	19	12	1.4	4.73	6	3	4.30	4.54	0.18	0.12
Karticpur	48	32	20	0.5	5.40	16	8	5.56	6.22	0.57	0.11
Chakrakona	69	13	18	0.6	5.70	10	6	1.50	1.75	0.06	0.08
Mohammedbazar	61	22	17	0.5	5.76	10	8	3.10	5.30	0.35	0.08

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phate-free and then washed with alcohol and benzene and finally dried in air at 40°C. The orange brown product was lightly ground in an agate mortar before use. Analysis showed that the product is a mixture of Fe (OH) and Fe $(H_2PO_4)_2$ and Fe $(H_2PO_4)_3$ in the following ratio $Fe_2O_3 : P_2O_5 = 1:2.5$.

Aluminium Phosphate: It was prepared by first precipitating aluminium hydroxide from potash alum with ammonia. Di-ammonium hydrogen phosphate was added to the washed hydroxide and the suspension was adjusted to pH 4 with phosphoric acid. The resultant product was washed free of phosphate with water and dried by washing with alcohol and benzene. The benzene was removed by air drying at 40°C. The final product, a white powder was lightly ground in an agate mortar and stocked. Its analysis showed $Al_2O_3 : P_2O_5 = 1: 1.9$, corresponding to $Al(OH) (H_2PO_4)^5$.

Amberlite OH-Resin: The commercially available Cl-resin was converted to OH-resin by treating with potassium hydroxide at first and then with 0.1 potassium hydroxide till the percolating solution was chlorine-free. It was washed with water till alkali-free, dried and stocked.

The experiment was laid out in two parts, viz. the iron and aluminium phosphates were allowed to react with (1) the acid soils and (2) OH-resin through the intermediary of a cellophane membrane.

Part 1. 0.1 g. aluminium phosphate was mixed with 5 ml. water in well-washed (with warm water) cellophane paper bags and then suspended into wide-mouthed 250 ml. bottles containing 10 g. of each soil sample separately in 100 ml. water. A similar set for each soil was also prepared with 0.1 g. iron phosphate. The pH of the suspensions were measured initially. The reaction was allowed to take place for 90 days with occasional shaking every day. At the end of the stipulated period, pH and phosphorus in the soil suspensions were determined.

Part 2. 0.1 g. ferric phosphate and 50 ml. water were taken in 3 separate 100 ml. beakers and the pH of the suspensions were adjusted to 4, 5 and 6 by means of 0.05 N potassium hydroxide and 0.05 (N) hydrochloric acid 1 g. OH-resin and 5 ml. water placed in well-washed cellophane paper bags was then suspended into each of the phosphate suspensions. The reaction was allowed to continue for 90 days with occasional shaking every day. The loss by evaporation of water in the beakers was maintained by adding requisite amounts.

Similar sets were prepared with aluminium phosphates. After 90 days of incubation, pH values of the suspensions were noted and the resin samples were removed into beakers and treated with 0.01 N potassium hydroxide to release phosphate, if any, that was exchanged for OH^-. The phosphorus in the potassium hydroxide solution was analysed.

Results and Discussion

Phosphorus released from the added iron phosphate and aluminium phosphates to soils is presented in Table 2. Soluble phosphorus increased in all the soils, more so in the Darjeeling soil (pH 4.73) during the period under study, possibly due to reduction of native iron phosphate and hydrolysis of iron and aluminium phosphates. Addition of iron phosphate increased soluble phosphorus by 4 to 22 ppm over control, highest being in the Mohammedbazar (pH 5.76) and lowest in the Darjeeling soil (pH 4.73).

Aluminium phosphate released more phosphorus than iron phosphate in the Darjeeling (pH 4.73) Karticpur (pH 5.40) and Chandrakona soils (pH 5.70) and equally effective in Mohammedbazar soil (pH 5.76). Soluble phosphorus increased by 6 to 22 ppm over control. The highest release of phosphorus from aluminium phosphate than iron phosphate may possibly be due to its increased solubility.

Soil pH increased in all treatments in all the soils. Simple submergence increased pH by 0.13 to 0.19 unit, highest being in the Karticpur soil and lowest in the Chandrakona soil. Addition of iron phosphate resulted

TABLE 2—RELEASE OF PHOSPHORUS FROM ADDED Fe-P AND Al-P TO SOILS IN 90 DAYS, ppm

Soil	Darjeeling			Karticpur			Chandrakona			Mohammedbazar		
	pH		P	pH		P	pH		P	pH		P
Treatments	Initial	Final		Initial	Final		Initial	Final		Initial	Final	
Soil + Water	4.75	4.92	14	5.43	5.62	10	5.73	5.86	8	5.80	5.94	10
Soil + Water + Fe-P	4.75	5.10	18	5.43	5.70	20	5.73	6.04	24	5.80	6.10	32
Soil + Water + Al-P	4.75	5.22	20	5.43	5.82	22	5.73	6.22	28	5.80	6.26	32

in rise in soil pH by 0.27 to 0.35 unit. However, the maximum rise is noted with aluminium phosphate ranging between 0.39 and 0.49 unit, highest being in the Chandrakona (pH 5.73 to 6.22) and lowest in the Karticpur (pH 5.43 to 5.82) soils.

It is indicated that the added iron and aluminium phosphates released phosphorus, more so at higher soil pH, thereby increasing the equilibrium concentration of soluble phosphorus and the processes responsible for this increase, reduction and hydrolysis, also increased the soil pH.

Table 3 shows the results obtained in the interaction of OH^- resin with the phosphates. The difference between aluminium and iron phosphates in releasing phosphorus is not marked, but the effect of pH is clearly indicated. In the control, iron phosphate hydrolyses to yield 120 ppm phosphorus during the period under study, with simultaneous rise in pH from 5.60 to 6.48. The release of phosphorus through the exchange of OH^- of resin is more effective at higher pH. Increase in pH of the exchange medium from 4 to 5 increased soluble phosphorus by 70 ppm and from pH 5 to 6, an increase of only 20 ppm P is noted.

TABLE 3—Release of Phosphorus from Fe-P and Al-P to OH-Resins in 90 Days, ppm

Treatments	pH		P	% of Total P released
	Initial	Final		
Fe-P + Water	5.60	6.48	120	6
Fe-P + Water + OH-resin	4.02	5.82	250	12.5
	5.04	6.24	320	16
	6.00	6.46	340	17
Al-P + Water	5.98	6.44	170	8.5
Al-P + Water + OH-resin	4.00	5.62	220	11
	5.04	6.46	340	17
	6.03	6.42	340	17

Similar results are also noted with aluminium phosphate. In the control, aluminium phosphate released 170 ppm phosphorus. Between pH 4 and 5, release of phosphorus is increased markedly to the extent of 120 ppm, but no such increase is noted between pH 5 and 6.

The release of phosphorus from these phosphates is accompanied by simultaneous rise in pH of the exchange medium. The pH of the phosphate suspensions adjusted to pH 4 are raised to about 5.70, but those adjusted to 5 and 6, attained nearly the same pH after equilibration for 90 days.

The observation that phosphorus released at higher pH is markedly greater than at lower pH, is in confirmity with what has been observed with the soil samples.

Acknowledgement

The author's thanks are due to Dr. S. N. Chakravarti, Presidency College, Calcutta for his keen interest.

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[Original mss. received on March 11, 1973]

UDC 631.416—1: 631.413.2

Application of four nitrogenous fertilizers to four types of soils showed that (i) black soil retained the maximum amount of ammonium ions from the added ammonium sulphate at all the doses whilst saline soil retained the least amount of added ammonium ions; (ii) in the case of ammonium chloride, the maximum retention of ammonium ions was observed in red soil at the lower dose; (iii) in the case of calcium ammonium nitrate, the red soil showed minimum retentive capacity, whilst black soil showed the maximum values, except being at 4 mg. nitrogen; (iv) black soil showed maximum ammonium retentive capacity on the addition of ammonium sulphate nitrate; and (v) the maximum fixation of added nitrogen took place in alluvial soil with all nitrogenous fertilizers whilst with other soils, the fixation varied with the nitrogenous fertilizer.

Retention and Fixation of Nitrogen Applied to Soils

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Introduction

When nitrogenous fertilizers are added to soils, they are likely to be retained in varying degrees (depending upon their nature) by the constituents of the soils allowing only a portion to remain in the free state to be directly utilized by the growing crops. It has been reported that clay content, the nature of the clay minerals present, pH, organic matter and cation-exchange capacity affect the retentive capacity of the soils for ammonium ions. The nitrate nitrogen, on the other hand, has been found to be extremely mobile and hence sometimes moves out of the root zone so as to become unavailable to plants.

Studies on the retention of added nitrogen for Indian soils are scanty. Sen[1], Ghildyal and Singh[2] and Grewal and Kanwar[3] have reported the absorption of ammonium nitrogen from different nitrogenous fertilizers using different soils. Sen[1] observed that the extent of absorption of ammonium nitrogen from ammonium chloride and ammonium sulphate is more or less similar in most of the soils, though a greater absorption takes place from ammonium chloride than from ammonium sulphate, thereby proving the superiority of the former over the latter.

Studies conducted by Allison[4] show that a fair part of the fixed nitrogen may become so chemically combined with the soil as to be unavailable to plants with the result that the response obtained from a given dose is partly reduced. Stevenson[5] observed that illite and related clays have significant ammonium-fixing capacity. In this fixed form, the nitrogen is not subjected to rapid oxidation, although it may become available at last. Bievre, Hende and Lox[6] found that 50 per cent of the added ammonium is unavailable to plants, if applied to clay soils. Only a small part of the labelled ammonium ions could be extracted. Prolonged application of fertilizers has been reported by Peterburgskii *et al*[7] to increase the amount of fixed ammonium without changing total ammonium-fixing capacity.

The fixation of ammonia by soils has been studied mostly under wet conditions. Peterburgskii and Korchangina[8] found that ammonium fixation is intensified if ammonium sulphate is applied to wet peat podzolic soils and heavy chernozems. However, Blasco and Cornfield[9] are of the opinion that no fixation of added ammonium by soil clays in Colombian soil takes place under wet condition. Page *et al*[10] have reaffirmed that fixation of ammonium takes place under wet condition and there is no reduction in the cation-exchange capacity of soils. Air-drying or oven-drying did not exceed the fixing capacity observed under wet condition.

Experimental

50 g. of black, red, saline and alluvial sufrace soil samples collected from the eastern part of U.P. (Meja,

Allahabad), were weighed in 250 ml. conical flasks and then 100 ml. of fertilizer solutions containing 6, 4 and 2 g. nitrogen from four fertilizers, viz. ammonium sulphate, ammonium chloride, calcium ammonium nitrate (CAN) and ammonium sulphate nitrate (double salt) were added. The contents were shaken for half-an-hour and left overnight. Next day, the liquid was separated from the soil through filtration using suction. The leachates were analysed for total ammonium ions by colorimetric method using Nessler's reagent (Jackson[11]).

The amount of ammonium retained by soils has been calculated from the difference in the amount of ammonium nitrogen originally added and the amount of ammonium nitrogen recovered in the leachates.

In order to determine the degree of ammonium-fixation, soils obtained after retention of ammonium ions were treated with 100 ml N sodium chloride solution (2.5 pH), shaken for half an hour and kept overnight. Next day, the soils were separated from the liquid by filtration and the leachates were analysed for exchangeable ammonium nitrogen by colorimetric method using Nessler's reagent (Jackson[11]).

The difference between the amount of retained ammonium and the ammonium extracted by N sodium chloride solution (2.5 pH) has been taken to be the amount of nitrogen present in the fixed form.

The per cent retention, fixation and exchangeable ammonium ions have been calculated on the basis of ammonium content alone of different fertilizers, while the nitrogen addition was made on the basis of the total nitrogen. Before using the fertilizers in different soils for the present study, soils and fertilizers were analysed for their chemical composition (Tables 1 and 2).

The results on the retention (R) and fixation (F) of nitrogen by soils have been reported in Table 3.

Results

The ammonium retentive capacity (ARC) of different soils (mg./50 g. soil) from ammonium sulphate, ammonium chloride, calcium ammonium nitrate and ammonium sulphate nitrate (Table 4) are evident from 'R' values given in Table 3. In the case of last two fertilizers, R values have been expressed in terms of their actual ammonium content and not on total nitrogen present in them.

TABLE 2—ANALYSIS OF DIFFERENT NITROGENOUS FERTILIZERS, %

Name of the Fertilizers	Estimated Total N, %	Form of N Total NH_4^+-N	NO_3^--N	NH_2-N	Guaranteed N
Amm. Sulphate	20	100	—	—	20
Amm. Chloride	25.7	100	—	—	26
Cal. Amm. Nitrate	19.5	50	50	—	20
Amm. Sulphate Nitrate	25.9	75	25	—	26

The data reported in the above table reveal that black soil retains maximum percentage of ammonium from added ammonium sulphate at all the three doses whilst the saline soil retains the least amount.

In the case of ammonium chloride the maximum retention of ammonium ions was observed in red soil at the lower doses. However, the magnitude of retention from ammonium sulphate and ammonium chloride is practically the same by all the soils. Sen[1] also observed a similar relation but he came to the conclusion that ammonium chloride was better fertilizer than ammonium sulphate.

In the case of calcium ammonium nitrate, the red soil shows minimum percentage retention of ammonium whilst black soil shows the maximum values (with one exception). Whereas black soil was seen having maximum ammonium retentive capacity at higher dose (6 and 4 mg.) on the addition of ammonium sulphate nitrate, but at lower dose (2 mg. N/50 g. soil) alluvial soil shows maximum ammonium retentive capacity.

From the data on the retention of ammonium ions by the four types of soils, it is observed that 'R' values depend upon (1) ammonium content of the fertilizers, i.e. the nature of the fertilizer, (2) the dose of nitrogenous

TABLE 1—CHEMICAL ANALYSIS OF THE SOILS USED

Soil Type	Total N, %	Available N, % NH_4-N	NO_3-N	Available P, %	Organic Carbon, %	pH	C.E.C., me/100 g.	$CaCO_3$, %	Total Salts, me/1.
Black	0.075	0.019	0.003	0.018	0.56	7.5	29.90	1.25	12.00
Red	0.042	0.005	0.001	0.024	0.30	6.8	11.48	0.00	2.87
Alluvial	0.052	0.012	0.002	0.022	0.45	7.4	9.48	2.75	3.54
Saline	0.071	0.015	0.003	0.034	0.51	7.6	7.58	0.75	55.87

TABLE 3—RETENTION AND FIXATION OF NH_4^+ FROM ADDED NITROGENOUS FERTILIZERS TO DIFFERENT SOILS

Soils	Black Soil					Red Soil				
Sources with Doses	Retained NH_4^+ Ions		Available E, mg.	Fixed NH_4^+		Retained NH_4^+ Ions		Available E, mg.	Fixed NH_4^+	
	R, mg.	% of added NH_4^+ Ions		F, mg.	% of added NH_4^+ Ions	R, mg.	% of added NH_4^+ Ions		F, mg.	% of added NH_4^+ Ions
N Added 6 mg.										
Amm. Sulphate	4.90	81.66	2.40	2.50	41.66	3.00	50.00	2.00	1.00	16.66
Amm. Chloride	4.60	76.66	2.80	1.80	30.00	3.80	63.33	1.80	2.00	33.33
Ca. Amm. Nitrate	2.30	76.66	1.80	0.50	16.66	1.00	33.33	0.65	0.35	11.66
Amm. Sulph. Nitrate	3.30	73.33	2.50	0.80	20.00	2.40	53.33	2.00	0.40	8.80
N Added 4 mg.										
Amm. Sulphate	3.90	97.50	2.20	1.70	42.50	2.40	60.00	1.40	1.00	25.00
Amm. Chloride	2.80	70.00	2.10	0.70	17.50	2.90	72.50	1.50	1.40	35.00
Cal. Amm. Nitrate	1.35	67.50	1.20	0.15	7.50	0.40	20.00	—	0.40	20.00
Amm. Sulph. Nitrate	2.20	73.33	1.10	1.10	36.66	2.20	73.33	2.20	—	—
N Added 2 mg.										
Amm. Sulphate	1.90	95.00	1.10	0.80	40.00	1.80	90.00	0.80	1.00	50.00
Amm. Chloride	1.90	95.00	1.20	0.70	35.00	2.00	100.00	0.70	1.30	65.00
Cal. Amm. Nitrate	1.00	100.00	0.80	0.20	20.00	0.90	90.00	0.20	0.70	70.00
Amm. Sulph. Nitrate	1.40	93.33	0.40	1.00	66.66	0.80	53.33	0.80	—	—
	Alluvial Soil					Saline Soil				
N Added 6 mg.										
Amm. Sulphate	4.20	70.00	1.70	2.50	41.66	2.80	46.66	2.00	0.80	13.66
Amm. Chloride	3.20	53.33	1.40	1.80	30.00	3.50	58.33	3.20	0.30	5.00
Cal. Amm. Nitrate	1.60	53.33	0.10	1.50	50.00	1.20	40.00	—	1.20	40.00
Amm. Sulph. Nitrate	2.50	55.55	1.10	1.40	31.11	2.40	53.33	0.40	2.00	44.44
N Added 4 mg.										
Amm. Sulphate	2.80	70.00	0.75	2.05	51.25	2.20	55.00	1.50	0.70	17.50
Amm. Chloride	1.90	47.50	0.65	1.25	31.25	2.00	50.00	1.80	0.20	5.00
Cal. Amm. Nitrate	1.60	80.00	—	1.60	80.00	1.35	67.50	—	1.35	67.50
Amm. Sulph. Nitrate	1.50	50.00	0.70	0.80	26.66	1.60	53.33	0.20	1.40	26.66
N Added 2 mg.										
Amm. Sulphate	1.90	95.00	—	1.90	95.00	0.80	40.00	0.20	0.60	30.00
Amm. Chloride	1.90	95.00	0.20	1.70	85.00	1.20	60.00	1.10	0.10	5.00
Cal. Amm. Nitrate	1.00	100.00	—	1.00	100.00	0.90	90.00	—	0.90	90.00
Amm. Sulph. Nitrate	1.50	100.00	—	1.50	100.00	0.70	46.26	—	0.70	46.65

NH_4^+ Ions present in the added amount of N fertilizers differ with N source. The % retention or fixation has been calculated on this basis alone.

Amount of N added	NH_4^+ present in N sources, mg.			
	Amm. sulphate	Amm. chloride	Cal. amm. nitrate	Amm. sulph. nitrate
6 mg	6	6	3	4.5
4 mg	4	4	2	3.0
2 mg	2	2	1	1.5

TABLE 4—ARC VALUES OF SOILS WITH DIFFERENT NITROGENOUS FERTILIZERS

Fertilizers	Ammonium Sulphate	Ammonium Chloride	Calcium Amm. Nitrate	Amm. Sulph. Nitrate
Black Soil	1.9-4.9	1.9-4.6	1.0-2.3	1.4-3.3
Red Soil	1.8-3.0	2.8-3.8	0.4-1.0	0.8-2.4
Alluvial Soil	1.9-4.2	1.9-3.2	1.0-1.6	1.5-2.5
Saline Soil	0.8-2.8	1.2-3.5	0.9-1.35	0.7-2.4

fertilizers added, and (3) characteristics of the soil used, i.e. the cation-exchange capacity (C.E.C.), the total carbon content, the clay content and soluble salts along with pH.

There is a tendency for ARC to increase as the dose of the fertilizers is increased from 2 to 6 mg. N/50 g. soil. This is due to greater number of ammonium ions being available for retention by soils.

The minimum and maximum retentive capacities of individual soils for ammonium ions vary in a wide range. It clearly points to the fact that the soils have inherent capacity to retain ammonium ions from fertilizers and the increase is not proportional to the increase in the doses of nitrogen that are being added. The ranges are briefly given in Table 5.

TABLE 5—ARC OF SOILS ON USING DIFFERENT NITROGENOUS FERTILIZERS

Black Soil	40-42	17-35	7-20	20.66
Red Soil	16-50	33-65	11-70	0-8
Saline Soil	13-30	5	40-90	26-46
Alluvial Soil	40-95	30-85	50-100	26-100

The colloidal surface (i.e. clay content) is, no doubt, responsible for the retention (surface adsorption) of ammonium ions but cation-exchange appears to be more prominent because ARC values of the soils follow their C.E.C. values. The presence of anions, viz. Cl^-, SO_4^{2-} and NO_3^-, in nitrogenous fertilizers used may also exercise their effect on retention. Ayers[12] has reported that sorption of ammonium and potassium ions was always greater with sulphate than with chloride. However, the role of anions in the present studies can be ascribed to be casual.

Exchangeable and Fixed Nitrogen: A part of the retained nitrogen (R) can be replaced by N sodium chloride (pH 2.5) whilst the rest remains with the soil. The fraction that is replaceable has been called exchangeable (E form) and the rest has been taken to be the fixed form (F). By changing the fertilizer in a soil, it is observed that the F values change. It will be logical to assume, therefore, that soils individually possess ammonium fixing capacities (AFC) just as they possess ammonium retentive capacities (ARC). The variation in AFC may be due to the clay mineral content of soils. The organic matter of soil may also help in keeping some ammonium in the fixed form. The ammonium fixing capacities of different soils are given in Table 5.

It is observed that the maximum fixation of added nitrogen is observed in the alluvial soil with all the nitrogenous fertilizers, whilst with other soils the values vary with nitrogenous fertilizers. For example, minimum fixation takes place in saline soil with ammonium chloride, whilst in red soil it is minimum with ammonium sulphate nitrate. In other words, for alluvial soil, all nitrogenous fertilizers are unsuitable because of high fixation of nitrogen. For red soil, the best fertilizer will be ammonium sulphate nitrate and for saline soil, ammonium chloride will be preferable and that too at the highest dose. The black soils are rich in montmorillonite, while the red soils in kaolinite clay minerals. If montmorillonite can fix the highest amount of nitrogen, as claimed by Blasco and Cornfield[9], then the black soil should top in nitrogen fixation. The effect of pH cannot be traced out from the present studies but according to Nammik[13] a low fixation will be observed with soil having a pH 5.7-5.8. Out of the four soils used, only the red soil has a pH less than 7.0. So far as the organic matter content is concerned, the saline soil with high carbon shows the least fixation; hence the role of carbon in fixing NH_4 cannot be claimed with certainty. The presence of soluble salts in saline soil may be responsible to an extent for retention and fixation of N. The clay content of the soils may also be assumed to play a part in fixation.

Significance of E/F: A perusal of the E/F ratios (Table 6) shows that there is a tendency for the ratios to increase as the amount of added nitrogen is increased from 2 to 6 mg. nitrogen per 50 g. of soil. Further, the ratios change with the sources of nitrogen as well as with the type of soil used. Low ratios are always obtained with all the fertilizers in all the soils at the lowest dose which clearly shows that the conversion of retained ammonium into F form is at its maximum and that E values are at their minimum. The ammonium containing fertilizers, however, are different from ammonium plus nitrate containing fertilizers, Thus, calcium ammonium nitrate shows highest F values in saline and alluvial soils, whereas in black soil the results are just the reverse, i.e. the conversion of retained ammonium to F form is at its

TABLE 6—RELATION BETWEEN EXCHANGEABLE (E) AND FIXED (F) FORMS OF NITROGEN (E/F RATIOS)

Black Soil				
6 mg.	0.96	1.55	3.60	3.12
4 mg.	1.29	3.00	8.00	1.00
2 mg.	1.37	1.70	4.00	0.40
Red Soil				
6 mg.	2.00	0.90	1.85	5.00
4 mg.	1.40	1.07	—	—
2 mg.	0.80	0.53	0.28	—
Alluvial Soil				
6 mg.	0.66	0.77	0.06	0.78
4 mg.	0.36	0.52	—	0.85
2 mg.	—	0.11	—	—
Saline Soil				
6 mg.	2.50	10.60	—	0.20
4 mg.	2.14	9.00	—	0.14
2 mg.	0.33	11.00	—	—

minimum. This is a salient feature which separates black soil from other soil types used in this study. The saline soil shows a similar behaviour with ammonium chloride. In other fertilizers, E/F ratios are practically similar in both alluvial and saline soils.

Discussion

Retention of Nitrogen: The term retention of nitrogen can be safely used to denote the removal of ammonium ions from the solution phase of nitrogenous fertilizers when added to soils. The fraction of retained nitrogen which is unavailable to plants may be termed as fixed form. However, there is a lot of confusion in the use of the terms retention and fixation of nitrogen by soils and usually fixation has been profusely used. Sorption and absorption have also been used at times.

The retention of ammonium ions can be explained to be due to cation-exchange in soils, which is dependent upon the number of ammonium ions available. The greater the number of ammonium ions present, the greater is the exchange, i.e. entry of ammonium ions into the exchange-complex of the soil. Consequently the retention of ammonium ions will be greater.

Fixation of Nitrogen: But the retention of ammonium though exchange does not stop here—the retained ammonium ions are converted into such forms as are not replaceable or available. This is called the 'Fixation' of ammonium ions or F form of nitrogen. In this process, the exchangeable ammonium ions (E form) get converted into non-exchangeable form (F form). The ammonium ions, thus, have a tendency to occupy such sites as are not approachable. This has been ascribed to be due to the entry of ammonium ions into the interlattices of the clay minerals. Especially, montmorillonite has been reported to fix a greater amount of ammonium ions (Blasco and Cornfield[9]). The black soil being rich in montmorillonite aptly fixes the maximum amount of ammonium ions. Thus, F will depend upon the nature and amount of clay minerals present in soils besides the initial concentration of ammonium ions that leads to a greater F value. The soils used in the present study have different clay minerals. The red soil contains mainly kaolinite, the saline soil both illite and kaolinite and the alluvial soil mixed clay minerals.

There is a further possibility of ammonium ions entering into organic combination. However, the soils do not vary much in their carbon content and hence no great variation can be expected.

The fixation of ammonium ions reported here is purely under wet condition and is further conditioned by the presence of such anions, like Cl^-, NO_3^-, and So_4^{2-}, and cations, like Ca^{2+} (in CAN). Due to the presence of cations, there is every likelihood of antagonism between Ca^{2+} and NH_4^+ ions leading to a lesser entry in the initial stage. The effect of pH and soluble salts cannot be clearly explained on the basis of these experiments.

One thing clearly brought about form F value is that a greater percentage of added ammonium ions is being transformed into the unavailable form at lower doses of nitrogenous fertilizer application. It points to the readiness with which ammonium ions can enter into the crystal lattices of clay minerals and get fixed. Such fixation may, thus, partly be responsible for the residual values of nitrogenous fertilizers.

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[Original mss. received on April 7, 1973]

UDC 633.523: 631.821.1: 631.85

A pot culture experiment was conducted to evaluate the performances of some water-insoluble phosphatic fertilizers relative to superphosphate on jute (*Corchorus olitorius* variety JRO 632) under limed and non-limed conditions in three acid soils. The overall effect of liming on yield of dry matter and total phosphorus uptake was significantly better in Nowgong and Sorbhog soils. Bud Bud soil, however, failed to respond to liming. In Nowgong soil, all the phosphatic sources, except Pelofos, significantly increased the total phosphorus uptake. In Sorbhog soil, the performance of Gafsa rock phosphate, Pelofos and Ultrafos were encouraging while in Bud Bud soil country basic slag was very effective. The water-insoluble phosphates compared very well with superphosphate in all the three soils.

Effect of Lime on the Performances of Different Phosphatic Fertilizers on Jute (*Corchorus Olitorius*)

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Introduction

Jute is one of the most important cash crops of India and a greater percentage of the jute-growing soils in the country are acidic in reaction. A considerable number of evidences indicate that in acid to neutral soils the water-insoluble phosphatic fertilizers are comparable to or even better than the water-soluble forms[1-3] and that application of lime to acid soils increases the availability of phosphorus to the crop.[4,5]

In view of the above considerations, the present investigation was undertaken to compare the effeciencies of basic slag and some rock phosphates relative to superphosphate under ordinary as also limed conditions in the acid soils of West Bengal and Assam.

Experimental

Pot culture experiments were conducted using surface soils (0-15 cm). collected from two jute-growing areas of Assam, viz. Nowgong and Sorbhog, and one of West Bengal, viz. Bud Bud (Table 1). Half of each soil was limed before 6 weeks from the time of sowing. Lime requirement to raise their pH near neutral was calculated according to Pratt and Bairs.[6] Six sources of phosphatic fertilizers @ 40 kg./ha of P_2O_5 with one control (no

TABLE 1—CHARACTERISTICS OF THE EXPERIMENTAL SOILS

Soil	pH		Available P_2O_5, kg./ha (Olsen's method)		Organic Carbon, % (Walkley & Black's method)	Available N, kg./ha (Alkaline $KMnO_4$ method)	Available K_2O, kg./ha (Ammonium acetate method)
	Limed	Non-limed	Limed	Non-limed			
Nowgong (S_1)	6.55	5.25	70.0	67.0	0.788	181.0	180.0
Sorbhog (S_2)	6.60	5.00	51.0	30.0	1.240	395.0	230.0
Bud Bud (S_3)	6.50	6.10	43.0	29.0	0.397	230.0	355.0

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phosphorus), thus making seven treatments, were included under both limed and non-limed conditions in each soil before sowing. The solubilities of each of these phosphatic sources are given in Table 2. The pots were arranged in split plot design with soil as main plot, liming as sub-plot and phosphatic sources as second order sub-plot treatments. Each treatment was replicated thrice.

TABLE 2—SOLUBILITY OF THE PHOSPHATIC FERTILIZERS USED

Fertilizers	Total P_2O_5, %	Citrate-Soluble P_2O_5, %
Superphosphate	17.80	2.28
Country basic slag	2.54	1.14
Pelofos	16.80	3.72
Ultrafos	28.60	12.66
Gafsa rock phosphate	29.00	11.42
Mussoorie rock phosphate	21.85	2.06

The test crop was *Corchorus olitorius* (var. JRO 632). The crop was sown on 21.4.69 and the plants were thinned to 6 per pot at the age of 4 weeks. The plants were harvested at 120 days' crop age and the yield of dry matter recorded. Soil analysis was done following conventional methods and total phosphorus uptake according to Koening and Johnson[7].

Results and Discussion

The effects of soil, liming and different phosphatic sources on the yield of dry matter and total phosphorus uptake by jute are presented in Tables 3-5.

The overall effects of three soils in increasing the yield of dry matter and total phosphorus uptake was by far the best in Nowgong followed by Sorbhog and Bud Bud. In both Nowgong and Sorbhog soils, liming significantly increased yield and phosphorus uptake. The very much better effect of liming in Sorbhog soil may be due to its

TABLE 3—EFFECT OF LIME AND SOIL ON YIELD OF DRY MATTER AND TOTAL PHOSPHORUS UPTAKE IN JUTE

Soil	Yield of Dry Matter, g./pot			Total Phosphorus Uptake, mg./pot		
	Limed (L)	Non-limed (NL)	Mean	Limed (L)	Non-limed (NL)	Mean
S_1	45.3	40.2	42.7	111.90	88.19	100.04
S_2	38.4	19.2	28.8	85.59	53.12	69.35
S_3	7.2	7.1	7.2	31.19	26.84	29.01
Mean	30.3	22.2	—	76.23	56.05	—
C.D. at 5% P						
for soil	2.3				3.54	
for lime	2.0				5.21	
for interaction S × L	3.4				9.05	

TABLE 4—EFFECTS OF LIME AND FERTILIZERS ON YIELD OF DRY MATTER AND TOTAL PHOSPHORUS UPTAKE IN JUTE

Fertilizers	Yield of Dry Matter, g./pot			Total Phosphorus Uptake, mg./pot		
	Limed	Non-limed	Mean	Limed	Non-limed	Mean
T_1 (Control)	24.7	20.3	22.5	63.50	49.81	56.66
T_2 (Super Phosphate)	33.7	22.3	28.0	81.86	53.73	67.79
T_3 (Country basic slag)	27.7	25.2	26.4	72.94	71.91	72.43
T_4 (Pelofos)	26.9	21.1	24.0	75.15	47.80	61.48
T_5 (Ultrafos)	33.6	19.5	26.5	78.06	55.66	66.86
T_6 (Gafsa rock phosphate)	33.2	20.3	26.3	77.34	57.69	67.51
T_7 (Mussorie rock phosphate)	33.2	26.5	29.9	84.73	55.74	70.23
Mean	30.3	22.2	—	76.23	56.05	—

C.D. (5%): Fertilizer—4.3
Interaction—Not Significant
L × T

Fertilizer—8.62
Interaction—12.23
L × T

TABLE 5—EFFECT OF SOIL AND FERTILIZER ON YIELD OF DRY MATTER AND TOTAL PHOSPHORUS UPTAKE IN JUTE

Fertilizers	Yield of Dry Matter, g./pot				Total Phosphorus Uptake, mg./pot			
	S_1	S_2	S_3	Mean	S_1	S_2	S_3	Mean
T_1 (Control)	35.2	25.7	6.7	22.5	80.40	62.16	27.41	56.66
T_2 (Super Phosphate)	49.6	28.3	6.1	28.0	110.82	68.39	24.16	67.79
T_3 (Country basic slag)	42.9	28.3	8.0	26.4	112.63	68.59	36.07	72.43
T_4 (Pelofos)	38.4	26.6	7.0	24.0	83.01	72.70	28.72	61.48
T_5 (Ultrafos)	40.7	30.8	8.2	26.5	99.22	71.58	29.79	66.68
T_6 (Gafsa rock phosphate)	42.6	29.2	7.0	26.3	99.99	74.16	28.38	67.51
T_7 (Mussorie rock phosphate)	49.7	32.7	7.2	29.9	111.24	67.90	28.55	70.23
Mean	42.7	28.8	7.2	—	100.04	69.35	29.01	—

C.D. (5%): Interaction—Not Significant
S × T

Interaction—14.97
S × T

low available phosphorus content. Despite the increase in pH and available phosphorus in Bud Bud soil due to liming, no increase in yield and total phosphorus uptake was noticed. Its poor fertility conditions as revealed by very poor organic matter content may be attributed to this failure to respond. A similar lack of beneficial effect of liming on paddy has been reported from Burdwan[8] and from the Central Nucleus Jute Seed Multiplication Farm, Bud Bud[9].

The performance of the phosphatic sources in increasing the yield of dry matter was as follows:

Treatments	T_7	T_2	T_5	T_3	T_6	T_4	T_1
Yield, g./pot	29.9	28.0	26.5	26.4	26.3	24.0	22.5

No significant difference was noticed between the water-insoluble and water-soluble forms though Mussoorie rock phosphate significantly increased the yield over Pelofos. As regards uptake of total phosphorus, no significant difference was found between the water-soluble and water-insoluble forms. Similar results were also obtained by Bill[10] and Ghosh[11], who concluded that in acid to near-neutral soils water-insoluble forms were not inferior but even superior to water-soluble forms. Under limed condition, the different phosphatic sources increased yield, though the yield differences were not significant. The interaction between phosphatic sources and lime with regard to total phosphorus uptake was significant as seen from Table 4. Country basic slag showed a significant increase in the uptake of phosphorus followed by Mussoorie rock phosphate. Though in the case of the other fertilizers the values were not significantly different from that of the control, in general their behaviour was found to be comparable to superphosphate. The superiority of basic slag in acid soils has been attributed to the presence of high amounts of silicate and lime[12], to the rise in soil pH and increase in ammonium and nitrate nitrogen as well as availability of phosphate to the crop[13]. Under limed condition, all the fertilizer treatments, except country basic slag, increased the total phosphorus uptake. In other words, liming did not improve the performanance of country basic slag. It may be presumed that due to the high calcium content of this fertilizer, further addition of lime to the soil along with it had no beneficial effect. On heavily limed soils, basic slag proved less effective than superphosphate[14].

An appreciable increase in yield of dry matter was obtained in S_1 and S_2 by Mussoorie rock phosphate and in S_3 by country basic slag and Ultrafos. In S_1, all the fertilizer sources, excepting Pelofos, significantly increased the total phosphorus uptake. In Sorbhog soil the performances of Gafsa rock phosphate, Pelofos and Ultrafos were encouraging while in S_3 country basic slag markedly increased the total phosphorus uptake, though the values did not reach the significant level (Table 4). The superiority of basic slag to other phosphatic sources in Bud Bud soil is in conformity with the findings of Goswami *et al*[15]. It is noteworthy that in all the three soils, basic slag and the rock phosphates were comparable to the water-soluble superphosphate. Thus, by the judicious use of lime, application of indigenous phosphatic sources can be made economical in the case of jute and the farmer can be gradually discouraged from using the more expensive superphosphate at least in the acid soils.

Acknowledgement

Thanks are due to Dr. N. N. Goswami, Senior Soil Scientist, I.A.R.I., for helpful discussions in planning the experiment.

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[Original mss. received on June 21, 1973]

UDC 545.37: 546.23: 546.24

A new amperometric method for the determination of selenium (IV) and tellurium (IV) with K-dithiotrihydroxymethyl aminomethane has been developed, using ammonium tartrate–potassium nitrate (pH 7.5) as the supporting electrolyte. The titrations were carried out at −0.2V vs S.C.E. at the dropping mercury electrode. The method is simple, precise and easily adoptable. The accuracy of the procedure is comparable with that of conventional methods.

An Amperometric Method of Determination of Selenium and Tellurium Using K-Dithiotrihydroxymethyl Aminomethane

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Usatenko *et al*[1] recommended the use of N-hyxyl and N-cyclopentyldithiocarbamates for amperometric titration of selenium and tellurium. The amperometric estimation of the two metals with potassium ethyl xanthate[2] and methyldithiobiuret[3] has been reported earlier from this laboratory. In the present investigation, K-dithiotrihydroxymethyl aminomethane has been used as an analytical reagent for the amperometric determination of selenium (IV) and tellurium (IV). The method is based on the measurement of the anodic current of excess titrating agent after the complete precipitation of the metal ion.

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Experimental

Reagents: The metal solutions of selenium (IV) and tellurium (IV) were obtained from E. Merck's sodium selenite and tellurite and standardized by the conventional method[4]. All other reagents used were of AnalaR variety.

Preparation and Standardization of K-Dithiotrihydroxymethyl

Aminomethane: 200 ml saturated solution of trihydroxymethyl aminomethane was taken in a pyrex beaker and 5/g. of caustic potash was added. After cooling the beaker in ice, 10 ml of carbon disulphide was added. The mixture was stirred thoroughly with a magnetic stirrer and the excess carbon disulphide removed by shaking thoroughly with double distilled pure benzene and the liquid was separated using a separating funnel. It was then evaporated a little by heating on a water bath and cooled in ice. Highly hygroscopic crystalline solid was separated. The reagent was standardized with potassium ferricyanide in alkaline medium in presence of osmium tetroxide as catalyst by amperometric titration at a potential of + 0.2V (vs SCE) using rotating platinum microelectrode.

Apparatus: The titrations were carried out in Fisher Elecdropode. Readings were taken using dropping mercury as the polarizable electrode. The non-polarizable reference electrode used was a saturated calomel electrode with Agar-KCl bridge. pH measurements were made with a line operated Beckman Zeromatic pH meter.

Procedure: The appropriate operative conditions for the quantitative estimation of selenium and tellurium by this reagent were established by trial experiments. It was observed that selenium can be determined quantitatively in a medium consisting of ammonium tartrate-potassium nitrate (overall concentration 0.15M-0.30M) within the pH range 7.0-8.5 and tellurium can be estimated in the same base electrolyte (overall concentration 0.01M to 0.05M) and pH adjusted between 7.0 and 9.0 (with ammonia) The final titration procedure adopted in each determination was more or less the same.

An aliquot of the metal ion was taken in a pyrex beaker containing 20 ml of the above buffer and pH of the solution was adjusted at 7.5 by adding aqueous ammonia. The titrations were carried out at an applied potential of —0.2V vs SCE with dropping mercury electrode. 2 ml microburette was used to deliver the titrant in small portions and the galvanometer reading was noted initially as well as after each addition of the titrant. After the complete precipitation of the metal ion, excess reagent gave the anodic diffusion current of its own resulting in a regular rise in the current. The plot of the volume of the reagent against the galvanometer reading is shown in Figs. 1 and 2 for selenium and tellurium respectively. The results of these titrations are given in Tables 1 and 2.

TABLE 1—Amperometric Determination of Selenium (IV) with H-Dithiotrihydroxymethyl Aminomethane

Base electrolyte concn.: 0.2 M ammonium tartrate + 0. 2 M potassium nitrate and ammonia, pH $\sim$ 7.5
Applied potential: —0.2V vs SCE
Indicator electrode: Dropping mercury electrode

Curve	Amount of Se (IV), mg.		% Error
	Taken	Found	
A	0.1776	0.1770	−0.34
B	0.3552	0.3552	—
C	0.5328	0.5368	+0.75
D	0.7108	0.7068	−0.36
E	0.8880	0.8808	−0.81

TABLE 2—Amperometric Determination of Tellurium (IV) with K-Dithiotrihydroxymethyl Aminomethahe

Base electrolyte concn. : 0.05 M ammonium tartrate + 0.05 M potassium nitrate and ammonia, pH $\sim$ 7.5
Applied potential: —0.2V vs SCE
Indicator electrode: Dropping mercury electrode

Curve	Amount of Te (IV), mg.		% Error
	Taken	Found	
A	0.2186	0.2186	—
B	0.4372	0.4354	−0.41
C	0.5465	0.5467	+0.04
D	0.6558	0.6531	−0.41
E	0.8744	0.8617	−1.45

Results and Discussion

The amperometric titration curves are reverse L shaped with a sharp break at the end-point which occurs at a stage when metal: reagent ratio is 1:4. Campbell and Reilley[5] have described the amperometric titration of

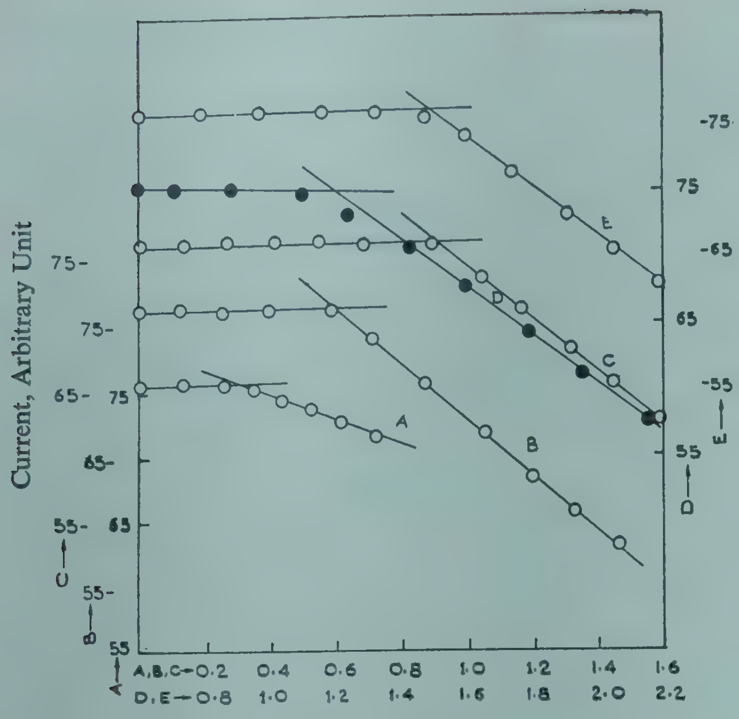

Fig. 1—Plot of Volume of Reagent Against Galvanometer Reading for Selenium

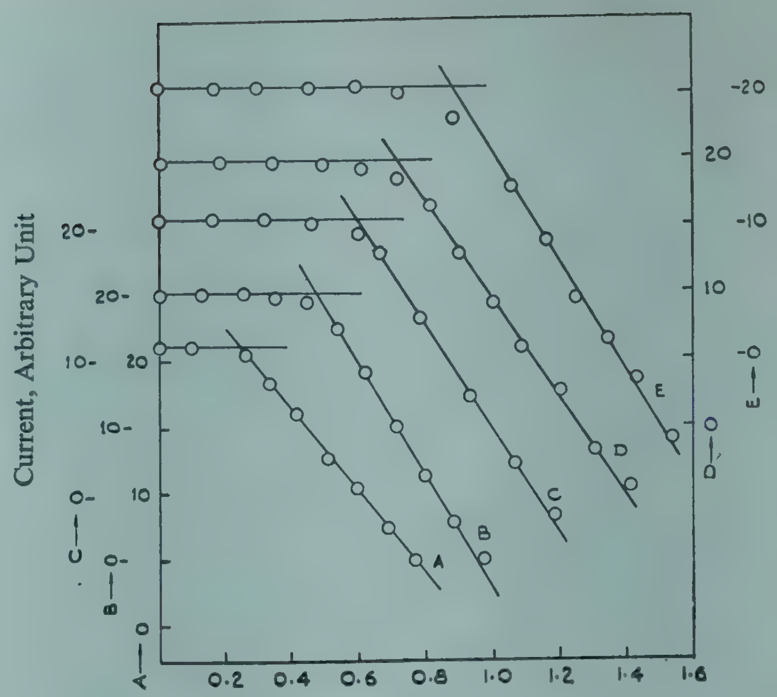

Fig. 2—Plot of Volume of Reagent Against Galvanometer Reading for Tellurium

milligram amounts of metal ions with chelating agent, the end-point being detected by means of the anodic wave of the chelating agent.

From the observed results it has been found that complex has the formula $[(CH_2OH)_3C\text{-}NH\text{-}C\text{-}S)]_4M$ where M = selenium or tellurium. The procedure is very rapid, as each determination requires only 5 min., very accurate and easily adoptable. It may be pointed out that the method is comparable with the other conventional procedures.

Acknowledgements

Sincere thanks are due to Prof. G. S. Deshkukh for helpful discussions and to the Council of Scientific and Industrial Research, New Delhi, for research grants.

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[Original mss. received on June 21, 1973]

UDC 631.841: 631.813

Fertilizer grade urea prills have been coated with hydrophobic substances, such as wax, PRP and stearic acid. The coated prills are not only found to be less hygroscopic but are less moisture-sensitive and remain free-flowing even at relatively high moisture content.

The Effect of Moisture on Coated Urea

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The prilling of highly concentrated solution or melt of urea with minimum water and only traces of free ammonia is a common feature with most of the modern urea processes. The prills thereby produced are non-porous, hard, spherical with smooth surface having excellent free-flowing characteristics. These prills do not normally require any conditioning treatment. Being hygroscopic urea needs protection from atmospheric humidity to keep the product in a free-flowing condition. The general practice is, therefore, to air-condition or dehumidify the silo where the fertilizer is stored in bulk and pack the product in moisture-proof bags prior to its dispatch to the consumers. These precautions are considered adequate. It has, however, been observed that in high humid regions even during short exposure that occurs when urea-filled moisture-proof bags are opened for distribution the fertilizer becomes moist and sticky causing considerable inconvenience during the distribution of the fertilizer in the fields. Moreover, the moist prills tend to stick to leaves of plants when the fertilizer is used for top dressing. Preference for the less hygroscopic ammonium sulphate for top dressing by the users under such climatic condition is thus understandable.

The present work was initiated with a view to protect the urea prills against the unavoidable exposure to humid atmosphere when the fertilizer is distributed in regions where high humidity prevails. One of the ways is to coat urea prills with suitable waxy substances which act as a barrier between the fertilizer and the humid atmosphere and thereby reduce the rate of its moisture absorption. Alternatively, fertilizer may be made less moisture-sensitive so that the moisture absorbed during short exposure does not cause undue deterioration in product quality. Both these characteristics are not as interrelated as is generally believed. The extent of moisture absorption by a fertilizer is shown[1] to be proportional to RH_A-RH_S (where RH_A is relative humidity of the atmosphere, RH_S relative humidity of the solution and is designated by CRH values of the fertilizer concerned). Thus, the hygroscopic behaviour is dependent on the soluble components of the fertilizers. The susceptibility or sensitiveness towards increasing moisture content, however, is dependent on the nature and amount of solution phase formed and its distribution pattern in or around the particles[2] which ultimately determine the extent of their adhesion.

A heavy coating of urea prills with sulphur[3] or wax[4] is claimed to make the fertilizer less hygroscopic. However, such products reduce the dissolution rate of urea in water and thereby control the release of nitrogen and are found useful mainly for the fertilization of turf grasses, forage crops and horticultural plants. Some patents have recently been taken and improvement in the quality of urea prills claimed using minimum quantity of coating material. Paraffin wax and soyabean oil[5] are stated to reduce the hygroscopicity of urea prills. A double coating of molten stearic acid and powdered kaolin[6] is claimed to make the fertilizer non-caking. In the present work, the effect of coating materials, viz. paraffin wax, petrolatum-rosin-paraffin wax (PRP) and stearic acid, on the hygroscopic behaviour and moisture sensitiveness of coated urea prills have been studied.

Experimental

Paraffin wax, stearic acid and PRP (1:1:1) as melt have been used for coating urea prills. The coating medium was then sprayed by compressed air through a nozzle over urea prills rotating in a small steel drum provided with baffles for showering action. All the samples were finally conditioned with 2 per cent kaolinite clay.

Hygroscopicity of the samples was determined by exposing the samples to 100 per cent R.H. and noting increase in weight at regular intervals.

Deterioration in samples with varying moisture content was studied by keeping samples containing varying moisture content undisturbed in glass containers for a period of one week and noting their condition everyday. During this period of incubation at room temperature the moisture absorbed on the surface of urea prills gets sufficient time to redistribute itself.

Results

The results on the study of hygroscopic behaviour and moisture sensitiveness of coated and uncoated urea prills are given in Table 1. The amount of moisture absorbed per unit area by the different samples at an interval of two hours have been recorded. There is no appreciable decrease in hygroscopicity of urea prills coated with 1 per cent stearic acid whereas there is a marked decrease in the hygroscopicity of urea samples coated with PRP. As expected an increase in the extent of coating decreased the hygroscopicity of the coated samples. With 2 per cent PRP, the decrease in the moisture uptake by coated urea prills is appreciable. The hygroscopicity of 2-3 per cent wax-coated sample was not, however, much different than that of uncoated sample.

When samples of urea containing 0.6, 1.0 and 2.0 per cent moisture were stored in stoppered glass bottles, it was found that all the samples were moist in appearance but the extent of interlinking of particles increased with an increase in the moisture content. Slight agglomeration was observed in samples containing 0.6 per cent moisture which became free-flowing after tapping. Samples containing 1 and 2 per cent moisture showed loss of free-flowing characteristics and the particles formed lump which did not break on tapping as indicated in Table 1. Urea prills coated with 1 per cent PRP remained free-flowing even with 2 per cent moisture. Urea prills coated with hydrophobic materials had a tendency to stick to each other. This was to a large extent overcome when 1-2 per cent coated material was further conditioned with 2 per cent kaolinite clay. Samples coated with 1 per cent stearic acid remained free-flowing upto 2.0 per cent moisture, though stearic acid as shown in Table 1 does not decrease hygroscopicity of urea. It was further observed that samples coated with 1 per cent wax remained free-flowing upto 0.6 per cent moisture but slight agglomeration was observed when the moisture was raised to 2 per cent. But samples coated with 2 or 3 per cent wax remained free-flowing upto 2.0 per cent moisture. It appears that hydrophobic film on urea

TABLE 1 HYGROSCOPICITY AND MOISTURE SENSITIVENESS OF COATED UREA

Sample	Coating on Urea		Hygroscopicity Amount of Moisture Absorbed, mg./sq. cm in 2 hr	Moisture Sensitiveness	
	Type	%		Moisture, %	Condition of the Product During one Week
1.	None	—	5.7	0.6	Moistness in the particles with slight agglomeration
		—	—	1.0	Lump formed
2.	Kaolinite clay	2.0	5.7	1.0	Slight agglomeration
		—	—	2.0	Lump formed
3.	Stearic acid	1.0	5.3	2.0	Free-flowing
4.	P-R-P	1.0	3.4	2.0	Free-flowing
5.	P-R-P	2.0	1.5	2.0	Free-flowing
6.	Wax	1.0	5.6	0.6	Free-flowing
		—	—	2.0	Slight agglomeration
7.	Wax	2.0	5.5	2.0	Free-flowing
8.	Wax	3.0	5.5	2.0	Free-flowing

All the coated samples were conditioned with 2 per cent kaolinite clay.

prills acts as abarrier and prevents direct contact between the particles and also affect the distribution of solution phase in a way which prevents agglomeration or interlinking of particles.

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[Original mss. received on June 15, 1973]

UDC 631.841.7: 631.894

Blendability of coated urea prills with granular TSP has been studied. The deterioration observed during storage of such a blend is significantly less than in a blend of granular TSP and uncoated urea prills. The effectiveness of various coating agents in minimizing the extent of deterioration is presented. The rate of deterioration, however, is found to increase with the amount of moisture content in TSP granules. Presence of free phosphoric acid in TSP improves to some extent the quality of coated urea–TSP blends.

Blendability of Coated Urea Prills with Triple Superphosphate

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The term, bulk blending, is defined as physical mixing of granular fertilizer materials, each of which contains one or two of the primary plant nutrients: nitrogen, phosphorus and potash. The keeping quality of the granular blends is superior to that of pulverized mixtures and bulk blends containing urea generally have good physical properties provided the presence of superphosphates and ammonium nitrate is avoided. In mixtures containing urea and superphosphates the free flowability is lost rapidly and the product becomes wet and sticky. This deterioration has been attributed to the formation of urea-monocalcium phosphate (MCP) adduct and consequent release of water of crystallization, as represented by the following equation:

$$4CO(NH_2)_2 + Ca(H_2PO_4)_2.H_2O$$
$$= Ca(H_2PO_4)_2.4CO(NH_2)_2 + H_2O$$

The released water forms saturated solution of soluble constituents, thereby generating enough liquid phase to cause stickiness and loss of free flowing characteristics.[1,2]

In our previous communication[3] an attempt was made to relate the deterioration of urea-TSP to the moisture and free acid contents of TSP. These tests were made with uncoated prilled urea. The present work relates to the study of the effect of coating urea with various coating agents to inhibit reaction with TSP.

Experimental

Fertilizer grade urea prills of $-10 + 16$ mesh (BSS) size were used in the present series of experiments. Such urea prills were coated with different hydrophobic coating materials such as petrolatum-rosin-paraffin wax (PRP), wax in linseed oil, wax alone and stearic acid.

Molten hydrophobic coating materials at a temperature of 80-85°C was sprayed by atomizing spray nozzles with compressed air heated to nearly 80°C on rolling bed of urea prills (45-50°C) in a small rotary drum. The product was then conditioned with 2 per cent kaolinite clay. Fully cured granular TSP with minimum amount of free phosphoric acid and of a similar size distribution as that of urea was used for blending. Free phosphoric acid in TSP was adjusted in various samples by adding the required amount of phosphoric acid. Subsequently the samples were dried. Moisture in coated prilled urea and TSP was adjusted by exposing the samples to 100 per cent relative humidity. In all the blends moisture content of urea was fixed at 0.5 per cent level.

Blended samples were kept in stoppered bottles and incubated at room temperature. Extent of deterioration of the samples was determined at regular intervals of time upto a period of 90 days from the day the constituents were blended. The various stages observed during the process of deterioration of the blend are characterized in the same way as in our previous communication[3], viz. stage 1, in which the blended product appeared dry and each granule showed free-flowing characteristics; stage II, some moistness and agglomerates appear; stage III, moistness increases as well as agglomerates; stage IV, completely sticky and pasty mass.

Results and Discussion

Incompatibility of urea and TSP blends is clearly evident from the results (Table 1) in which blend of uncoated urea (0.5 per cent moisture) with TSP containing only traces of free phosphoric acid and 2.0 per cent moisture deteriorates rapidly and the product becomes completely moist and pasty (IV stage) on the 3rd day. Marked improvement occurred when urea was coated with 1 per cent PRP. Coated urea when blended with TSP containing 4 per cent moisture and 2 per cent phosphoric acid, the product remained free flowing for more than a month (Table 1; blend 2).

Some samples were prepared by coating urea with molten paraffin wax (m.p. 60°C) alone and some with wax and linseed oil. For proper coating of molten wax it was found necessary to use hot compressed air to avoid premature solidification of wax. Wax and linseed oil could be coated with unheated compressed air. Contrary to expectations, a quick drying oil like linseed oil in combination with wax was not found to be very effective. Though wax-linseed oil coating gave a product whose particles do not stick to each other and dusting with 2 per cent kaolinite clay was in fact not necessary. The results with 2 per cent wax coated urea samples when blended with TSP containing 2-4 per cent moisture and 2-4 per cent free acid remained free flowing up to a period of 50 days after being mixed. Results further reveal that the extent of deterioration of the coated urea–TSP blend was dependent on the moisture content of TSP.

The improvement observed in the storage behaviour of the blends that contain urea prills coated with hydrophobic materials is clearly evident from the results given in Table 1. This arises as the film of hydrophobic materials on the surface of the urea prills prevents direct contact between the constituents and thereby interferes in the adduct formation. In addition the distribution pattern of solution phase on the surface of coated urea prills changes in a way that diminishes extent of inter-

TABLE 1—CHARACTERISTICS OF COATED UREA AND TSP BLENDS

Blend	Coating on Urea		T.S.P.		Days for Physical Condition to Reach Indicated Stage		
	Type	%	Moisture, %	Free Acid, %	Stage II	Stage III	Stage IV
1.	None	—	2.0	—	1	2	3
2.	P-R-P	1	4.0	2.0	36	45	60
3.	Wax	1	2.0	2.0	4	10	18
4.	Wax	2	2.0	4.0	71	—	—
5.	Wax	2	4.0	4.0	50	60	70
6.	Wax	3	2.0	4.0		No deterioration.	
7.	Wax	3	4.0	4.0	36	90	—
8.	Wax	4	2.0	4.0		No deterioration.	
9.	Wax Linseed oil	1 2	3.0	—	39	43	47
10.	Stearic acid	1	4.0	—	21	29	42

All the coated urea samples were further conditioned with 2 per cent kaolinite clay.
Urea prills contained 0.5 per cent moisture.

linking between particles. This factor is responsible for superior free flowing characteristics of urea prills even at relatively high moisture content[4]. Both these factors are likely to contribute to the improvement observed when coated urea is blended with TSP.

The results further showed that the rate of deterioration is dependent on the moisture content of TSP used in the blend. This may be explained thus: The first step in the deterioration of the blend involves the transfer of moisture through vapour phase or direct contact from TSP containing 2-4 per cent moisture to coated urea. Vapour phase transfer of moisture would depend on the vapour pressure difference of the two components. Direct transfer of solution phase due to interparticle contact is also expected. When coated urea prills gain moisture at the expense of TSP, the moisture, as a saturated solution of urea, resides on the surface of the prill due to its non-porous nature. The saturated solution of urea then dissolves MCP and the adduct is formed and water is liberated which in turn dissolves more of urea and more adduct formation occurs. This process continues till the blend becomes completely moist and pasty and stage IV is reached. Relatively slower rate of deterioration was consistently observed with coated urea–TSP blends in which TSP contained free phosphoric acid. The presence of free phosphoric acid in TSP reduces the vapour pressure and thereby the vapour phase transfer of moisture from TSP to urea is delayed or prevented depending on the phosphoric acid water ratio present in TSP. Only direct transfer of moisture due to interparticle contact occurs. Hence the deterioration is inhibited in presence of free phosphoric acid.

Thus, coated urea prills can be blended with TSP and stored for a limited period of time before its application in the fields. This is not possible with uncoated urea as the deterioration of the blend starts soon after its mixing and becomes unmanageable within 48 hours.

Acknowledgement

Authors are indebted to the referee, Dr. George Hoffmeister of TVA (USA), for many useful suggestions that have been incorporated in this paper.

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[Original mss. received on June 15, 1973]

UDC 541.128: 545.223: 546.3

Using ammonia-ammonium bifluoride as buffer, a rapid iodometric method of estimation of zinc as well as zinc, copper and iron in mixtures has been developed. This method has been extended to the estimation of zinc, copper and iron in low temperature co-conversion catalyst with satisfactory results.

A Rapid Method for Iodometric Estimation of Copper, Iron and Zinc in L. T. Shift Catalyst

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Application of an iodometric method for the estimation of copper is well-known[1–2]. The methods for the estimation of copper and iron in a mixture have also been reported[3–4]. A method for the estimation of zinc by iodometric titration, first proposed by Lang[5], was investigated along with others by Mann and Swift[6]. The method involves addition of an excess of ferricyanide and iodide to a solution of zinc, whereupon iodine is liberated as a result of combination of precipitation and oxidation-reduction reactions, which can be expressed by the following overall equation.

$$3Zn^{2+} + 2K^+ + 2Fe(CN_6)^{3-} + 3I^- = K_2Zn_3[Fe(CN)_6]_{2(S)} + I_3^- \qquad (1)$$

Mann and Swift[6] used pthalic acid monohydrate-pthalate or sulphuric acid-sulphate as buffer to adjust the pH of the test solution and reported the optimum pH for titration as 3.0. They found it necessary to increase the calculated value of zinc by an empirical factor of 1.019 to get the correct amount of zinc.

None of the iodometric procedures, reported in literature, have been found suitable for estimating zinc in presence of copper and iron. In the present communication, iodometric procedures for the estimation of zinc when present alone, as well as of copper, iron, and zinc in mixtures have been described. The use of ammonia and ammonium bifluoride, instead of pthalic acid-pthalate or sulphuric acid-sulphate as buffer, has been found advantageous because the rate of liberation of iodine in the system is quicker, end point more sharp and masking of iron by bifluoride makes titration of copper and zinc possible in the same solution. Aluminium chloride, added after titration of copper to demask iron before its titration, produced sufficient hydrochloric acid to prevent hydrolysis of iron. Cuprous iodide formed during the titration of copper accelerates the reaction.

$$2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2 \qquad (2)$$

Zinc does not interfere in the estimation of copper and iron. The results of analyses of synthetic solutions of zinc as well as of copper, iron and zinc in mixtures (Tables 1 & 2) with widely varying concentrations and ratios are found to be within limits of analytical error. Analyses of five low temperature shift catalyst samples (Table 3) by the procedure described below and also by the conventional method show that the maximum percentage deviations are 0.05 for iron, 0.09 for copper and 0.25 for zinc. Moreover, the recommended procedure avoids the use of any empirical correction factor for zinc, found necessary by Mann and Swift[6].

The time required for analysis by the recommended procedure is only 1 hr. as against 7 to 8 hr. by conventional method.

Experimental

Reagents

A. R. Grade chemicals were used to prepare the following solutions (aqueous, w/v): potassium iodide (20 per cent), aluminium chloride (10 per cent), ammonium bifluoride (10 per cent), potassium ferricyanide (5 per cent), starch (0.5 per cent), nitric acid (1:1), hydrochloric acid (1:1), ammonia (5 per cent), 0.1 N sodium thiosulphate.

Standard Solutions of Copper, Zinc and Iron

Copper: 6.636 g. of pure copper foils were dissolved in excess nitric acid, boiled to expel the nitrous fumes, transferred to one litre volumetric flask, and the volume made up to the mark with distilled water at room temperature. Each ml of the solution contained 6.636 mg of copper.

Zinc: 10.06 g. of pure zinc shots were dissolved in nitric acid, and the solution prepared as in the case of copper. Each ml contained 10.06 mg. of zinc.

Iron: Weighed quantity of ferric nitrate was dissolved in distilled water and made up to 1 litre in a volumetric flask. Iron content of the solution was estimated by standard method and each ml of the solution was found to contain 4.84 g. of iron.

Stock Solutions of Catalyst Samples

Five stock solutions of commercial low temperature shift catalysts were prepared by digesting in each case about 2.5 g. of powdered catalyst samples with 15 ml. of 1:1 dil hydrochloric acid and 5 ml. 1:1 dil nitric acid.

TABLE 1—DETERMINATION OF ZINC (SYNTHETIC SOLUTION)

Expt.	No.	Zinc Taken, mg.	Zinc Found, mg.	% Deviation
1.	a	10.06	10.07	+0.09
	b	"	"	"
	c	"	"	"
2.	a	25.15	25.16	+0.04
	b	"	"	"
	c	"	"	"
3.	a	50.30	50.28	−0.04
	b	"	"	"
	c	"	"	"
4.	a	100.60	100.56	−0.04
	b	"	"	0.04
	c	"	100.53	−0.07
5.	a	150.90	150.81	−0.06
	b	"	"	0.06
	c	"	150.80	−0.07
6.	a	201.20	200.65	−0.27
	b	"	200.84	−0.17
	c	"	"	0.17
7.	a	251.50	250.80	−0.27
	b	"	250.80	−0.27
	c	"	250.65	−0.33

TABLE 2—DETERMINATION OF COPPER, IRON AND ZINC (SYNTHETIC SOLUTION)

Expt. No.	Copper Taken, mg.	Copper Found, mg.	Iron Taken, mg.	Iron Found, mg.	Zinc Taken, mg.	Zinc Found, mg.	% Variation		
							Copper	Iron	Zinc
1	13.27	13.26	4.840	4.85	50.30	50.35	−0.07	+0.20	+0.09
2	33.18	33.20	9.680	9.66	50.30	50.25	+0.06	−0.20	−0.09
3	33.18	33.16	9.680	9.66	100.60	100.65	−0.06	−0.20	+0.05
4	66.36	66.48	29.040	29.10	100.60	100.55	+0.18	+0.20	−0.05
5	66.36	66.48	48.400	48.42	150.50	150.32	+0.18	+0.04	−0.12
6	99.54	99.85	48.400	48.54	150.50	150.32	+0.31	+0.12	−0.12
7	99.54	99.78	72.650	72.72	201.20	201.00	+0.24	+0.09	−0.09
8	199.08	199.50	96.960	100.25	251.50	250.68	+0.21	+0.30	−0.32

TABLE 3—ESTIMATION OF COPPER, IRON AND ZINC IN L.T. CO-CONVERSION CATALYST

Sample No.	% Copper (Iodometrically)	% Copper (By Conventional method)	% Iron (Iodometrically)	% Iron (By Conventional method)	% Zinc (Iodometrically)	% Zinc (By Conventional method)	% Variation		
							Copper	Iron	Zinc
1	25.75	25.76	1.68	1.68	47.53	47.40	+0.01	−0.00	−0.13
2	25.43	25.45	1.64	1.68	46.71	46.90	+0.02	+0.04	+0.19
3	25.43	25.38	1.43	1.45	43.61	43.45	+0.05	+0.02	−0.16
4	26.62	26.58	1.27	1.25	45.18	45.38	+0.04	−0.02	+0.20
5	25.77	25.68	1.65	1.68	47.28	47.05	+0.09	+0.03	−0.23

The solutions were evaporated to dryness, redissolved in 15 ml of 1:1 dil hydrochloric acid, boiled for a few minutes, filtered to separate insoluble materials, transferred to 500 ml volumetric flasks and the volumes made up with distilled water at room temperature.

Recommended Procedures

Estimation of Zinc in Synthetic Solutions: A known volume of a standard zinc solution was taken in a conical flask, and diluted to about 100 ml with distilled water. Dilute ammonia solution was added to the solution drop by drop until the precipitate of zinc hydroxide just appeared; then a solution of ammonium bifluoride was added to dissolve the precipitate and to adjust the pH between 3.5 and 4.0. Finally 15 to 20 ml of potassium iodide and 5 ml of potassium ferricyanide solutions were added and the flask after a few swirling motions was kept in the dark for 5-6 min. The liberated iodine was titrated with 0.1 N sodium thiosulphate solution with starch as indicator until a distinct yellow colour of ferricyanide appeared.

The procedure was carried out with different known quantities of standard zinc solution and seven sets of results have been tabulated (Table 1). The amounts of zinc in all the cases were calculated from the stoichiometry of equation (1).

Estimation of Copper, Iron and Zinc in Synthetic Mixtures: Eight synthetic solutions of copper, iron and zinc in different ratios (Table 2) were prepared by mixing and diluting calculated volumes of all the three standard solutions in volumetric flasks. Two aliquots of each of these synthetic solutions, containing known amounts of copper, iron and zinc were taken for each experiment, one for the estimation of copper and iron and the other for zinc.

Copper and Iron: To the aliquot diluted to a volume of 100 ml. in a conical flask dil. ammonia solution was added until the precipitates of hydroxides just appeared. Ammonium bifluoride was then added to dissolve the precipitates and adjust the pH between 2 and 3, whereby iron was masked completely. 20 ml of potassium iodide was added to the solution and the liberated iodine was titrated with 0.1 N sodium thiosulphate solution till the iodine colour is perceptible; 5 ml of starch and 2 to 4 ml of potassium thiocyanate solutions were then added and the titration continued to the iodine-starch end point. The amount of copper was calculated from the volume of 0.1 N sodium thiosulphate consumed. After titration of copper 20 ml of aluminium chloride solution, 0.2 to 0.3 gm. of sodium bicarbonate and 5-10 ml potassium iodide solution were added to the solution which after a few swirling motions was kept in the dark for 5 to 6 min. The liberated iodine was then titrated with 0.1 N sodium thiosulphate with starch as indicator. Amount of iron was calculated from the volume of 0.1 N sodium thiosulphate consumed. The amounts of copper and iron calculated from the volumes of 0.1 N sodium-thiosulphate consumed have been tabulated in Table 2.

Zinc: To the second aliquot, diluted to a volume of about 100 ml in a flask, 5 ml of ammonium bifluoride was added to mask iron completely. The pH of the solution was adjusted between 3.5 to 4.0 by alternate addition of dilute ammonia and ammonium bifluoride solutions. 20 ml of potassium iodide was then added and the liberated iodine titrated with 0.1 N sodium thiosulphate to the conventional starch-iodine and point for copper.

The titrated solution was then filtered and filtrate collected in a 250 ml conical flask after a thorough washing of the precipitate with cold water. To the filtrate in the flask 20 ml of potassium iodide and 5 ml of potassium ferricyanide were added and after a few swirling motions, was kept in the dark for 5 to 6 minutes. The liberated iodine was then titrated with 0.1 N sodium thiosulphate solution until the blue colour of iodine-starch disappeared and distinct yellow colour of ferricyanide persisted. It has been observed that when zinc is the predominant constituent of the mixture and percentages of iron and copper do not exceed 5 and 30 respectively, zinc can be titrated in the same solution without prior separation of cuprous iodide precipitate after titration of copper. The estimated amount of zinc in all the experiments along with actual amounts present in all the cases have been shown in Table 2.

Estimation of Copper, Iron and Zinc in Catalyst Samples: Aliquots of stock solutions of catalyst samples were taken, and copper, iron and zinc were estimated following the procedure already described. The catalyst samples were also analysed for copper, iron and zinc by the conventional method. The results of all these estimations are given in Table 3.

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[Original mss. received on July 7, 1972]

UDC 541.128: 546.72−31+546.76−31

The promoter action of chromia for water gas shift reaction was investigated by its incorporation into ferric oxide using different chromium compounds. The incorporation in each case was effected by intimate mechanical mixing. The activity tested at 350 and 450°C using the gas mixture (in percentage), carbon monoxide 30, carbon-dioxide 10-11, hydrogen 38 and rest nitrogen, and an equivalent amount of steam at a dry gas space velocity of 2000 hr^{-1} showed that chromia obtained from chromium acetate gives a catalyst having the maximum specific activity and low apparent density. The strength was, however, comparatively low. Regarding activity, ammonium dichromate and chromate were found more suitable than chromic acid. The effect of *in situ* formation of ammonium dichromate and chromate using a mixture of chromic acid and an equivalent amount of ammonium bicarbonate was also investigated. The incorporation of chromium compounds by preparing *in situ* was found to yield a catalyst having a slightly higher activity and lower apparent density. The physical properties of the samples, in general, were consistent with the results of activity.

Effect of the Preparative Conditions of Chromia on its Promoter Action in Water Gas Shift Reaction

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Ferric oxide-chromia catalyst is normally used for the water gas shift reaction in the range 350-500°C. Ferric oxide is the active component and chromia acts as the promoter[1,2], the function of the latter being arresting the grain growth of ferric oxide during its reduction to Fe_3O_4[3,4]. It is, therefore, expected that activity and stability of ferric oxide-chromia catalyst may be influenced by the mode of dispersion of chromia in the system. The present endeavour is to study the influence of dispersion of chromia in the system by incorporating it using different chromium salts, viz. chromium acetate, ammonium chromate and ammonium dichromate, and also chromic acid. Though the final product of decomposition of all the above substances is chromia, the modes of thermal decomposition, as well as the product gases differ from one another. Chromium acetate decomposes at 320-340°C to give chromia, water and carbon oxide; the decomposition of ammonium chromate and dichromate gives rise to chromia nitrogen, ammonia and water and chromia nitrogen and water respectively at 200-230°C. Chromic acid, however, decomposes around 400°C, yielding threby chromia, oxygen and water. It is expected that the nature of the evolved gases and their respective rates of liberation will influence the structure and texture of the catalyst[5,6]. Consequently, the incorporation of chromia using the above different salts is likely to play some role in determining the physical characteristics of the catalyst *vis-a-vis* their activity for converting carbon monoxide into dioxide. Although the use of different chromium compounds is reported earlier[6–10], yet no comparative study using different chromium compounds in ferric oxide-chromia has been made so far.

Experimental

Preparation of Samples: Precipitated iron oxide obtained by the reaction of ammonium bicarbonate with ferrous sulphate was heated at 300°C. The latter was pulverized to 100 mesh (BSS) size in a ball mill and then intimately mixed with different chromium compounds and chromic acid (as the case may be) in a kneader for about 4 hr. in each case so that a uniform and moderately hard paste is obtained. The quantity of water used during mixing was the same in all the cases. The paste was sprayed to a thickness of 6 mm. and dried in an air-oven at 110±10°C for 12 hr to reduce the moisture content to about 4-5 per cent. The dried material was granulated to about 1-2 mm size and pelleted with 1-2 per cent graphite to 6×6 mm size.

In another set of samples (Table 1), ammonium chromate and dichromate were prepared *in situ* using chromic acid and an appropriate quantity of bicarbonate in the kneader. The samples were designated as B_1, B_2, B_3 and B_4 for mixing with different chromium compounds, viz. chromic acid, ammonium dichromate, ammonium chromate and chromium acetate, respectively. For the samples B_5, B_6, B_7, B_8 and B_9, chromic acid was used and 5, 10, 20, 25 and 30 per cent of ammonium bicarbonate were added respectively during the kneading.

Determination of Physical Parameters: (1) **Bulk Density**—It was determined in the usual way. (2) **Crushing Strength**—It was determined with a tensometer by applying a fixed load and calculating the average strength using 10 pellets for each sample. (3) **Surface Area and Porosity**—These were determined by the BET[11] method using liquid nitrogen at —189°C and by helium displacement respectively.

Activity: Semi-water gas of the following average composition (in percentage), viz. carbon dioxide 8-10, carbon monoxide 28-30, oxygen 0-0.2, hydrogen 35-40 and nitrogen 20-25, was saturated by passing through a saturator in which water was maintained at a suitable temperature to get a steam-to-gas ratio of 1.0 at the inlet to reactor. This saturated gas was preheated and passed over the catalyst at a dry gas space velocity of 2000 hr^{-1} and activity was measured at 350 and 450°C. The activity has been expressed as percentage conversion of carbon monoxide to dioxide and calculated using the expression

$$\frac{\text{Outlet } CO_2\text{—Inlet } CO_2}{(100\text{-outlet } CO_2)} \times \frac{100}{\text{Inlet CO}}$$

Results and Discussion

The results of bulk density and crushing strength are given in Table 1 along with chemical composition and the physical parameters in Table 2. Table 3 gives the activity results of the samples. For the sake of convenience of discussion, samples have been divided into two series,

TABLE 1—COMPOSITION AND PROPERTIES OF CATALYST SAMPLES

Sl. No.	Sample No.	Bulk Density, g./cc.	Strength Fresh, kg./cm².	Chemical Composition, %.		
				Fe_2O_3	Cr_2O_3	LOI at 900°C
1.	B_1	1.40	140	86.20	9.58	4.02
2.	B_2	1.25	106	86.60	9.54	3.76
3.	B_3	1.30	113	86.22	9.42	4.28
4.	B_4	1.16	94	87.21	9.67	3.23
5.	B_5	1.18	98	86.62	9.81	3.51
6.	B_6	1.18	98	86.45	9.62	4.08
7.	B_7	1.20	96	87.10	9.81	3.32
8.	B_8	1.21	92	87.25	9.67	3.14
9.	B_9	1.20	90	86.63	9.84	4.58

TABLE 2—PHYSICAL PARAMETERS OF FRESH CATALYST SAMPLES

Sl. No.	Sample No.	BET Surface Area, m²/g.	Total Pore Volume, cc./g.	Pore Size Distribution, Å					
				4-175	175-200	200-300	300-400	400-500	500-75,000
1.	B_1	22.3	0.2421	19.1	4.5	19.1	19.1	15.2	23.0
2.	B_2	33.5	0.2827	28.9	6.3	16.3	11.0	9.5	28.0
3.	B_3	26.7	0.2695	20.3	4.2	16.7	13.2	9.0	36.6
4.	B_4	24.7	0.2280	11.2	3.6	10.1	6.4	5.5	62.5
5.	B_5	30.2	0.2911	32.1	2.9	14.9	10.7	9.5	29.9
6.	B_6	32.8	0.3848	34.8	2.9	9.1	6.6	0.8	45.8
7.	B_7	30.2	0.3382	32.7	4.1	11.7	9.3	8.2	34.0
8.	B_8	28.8	0.2882	26.9	6.4	15.6	12.0	8.2	30.9
9.	B_9	27.2	0.2632	25.9	4.1	14.5	10.3	8.3	24.9

TABLE 3—CONVERSION EFFICIENCY OF CATALYSTS

Sl. No.	Sample No.	Reaction Temp, °C	Hours of Run	% CO Inlet	% CO in Converted gas	% CO Conversion
1.	B_1	350	4	29.8	6.6	71.8
		450	10	29.8	5.8	75.2
2.	B_2	350	4	30.0	6.4	73.6
		450	10	29.8	5.4	77.4
3.	B_3	350	4	29.8	6.2	74.1
		450	10	29.6	5.2	79.0
4.	B_4	350	4	29.6	4.8	79.1
		450	10	29.6	4.4	82.4
5.	B_5	350	4	29.6	8.4	64.6
		450	10	29.0	5.4	77.5
6.	B_6	350	4	29.4	6.6	71.6
		450	10	29.4	5.0	80.0
7.	B_7	350	4	29.6	6.4	72.[illegible]
		450	10	29.8	4.6	81.8
8.	B_8	350	4	29.6	6.8	71.1
		450	10	29.4	5.6	77.2
9.	B_9	350	4	29.8	6.8	70.8
		450	10	29.8	5.8	76.2

viz. (i) those prepared with different chromium compounds using nitric acid as binder and, (ii) others prepared using chromic acid and ammonium bicarbonate, the latter having been used in different percentages.

Bulk Density and Mechanical Strength: It appears from the results that the mechanical strength of the pellets depends on the nature of chromium compounds used. Chromic acid appears to impart the highest mechanical strength whereas chromium acetate seems to contribute little to the strength. The other chromium compounds, viz. chromate and dichromate, gave a moderate to fair strength to the finished pellets. The influence of the compounds on the mechanical strength was clearly reflected in the respective parent densities of the finished pellets (Table 1). The sample prepared from chromic acid has the highest bulk density and that obtained with the chromium acetate the lowest. This can be explained by the reasoning that the oxidizing nature of chromic acid contributes towards better mechanical strength, whereas liberation of large quantities of non-oxidizing gases from the other compounds during their decomposition makes them highly porous resulting in low bulk density and lower mechanical strength. Chromate and dichromate, by virtue of their oxidizing nature, try to impart some mechanical strength but the latter is partly affected due to the liberation of large quantities of non-oxidizing gases, thereby making the product highly porous.

Surface Area and Porosity: From Table 2, one does not fail to observe that the surface area is highest when ammonium dichromate was used for the incorporation of chromia and the same is comparatively low when chromic acid was used. Surface areas of samples prepared from ammonium chromate and chromium acetate are also low. This can be explained by reasoning that the evolution of ammonia and carbon dioxide respectively from chromate and chromium acetate creates a preponderance of larger pores compared to that from ammonium dichromate, in which case evolution of nitrogen probably creates comparatively small pores by virtue of the latter's smaller molecular diameter. The lower surface area of the sample, prepared using chromic acid, can be accounted for if the sintering effect on ferric oxide is considered due to the formation of chromia from chromic acid at a comparatively high temperature[5] (400°C). In the cases of samples B_2, B_3 and B_4, chromia is formed at an early stage to protect at least partially the sintering of the active component ferric oxide. The percentage of smaller pores, i. e. up to 300°A, shows a similar trend.

The percentage of pores in this range is about 52 per cent in case of sample B_2 prepared using dichromate, and it is about 42 per cent for B_1 and B_3. The low percentage of smaller pores (26 per cent) for B_4 prepared using chromium acetate cannot, however, be explained from the present data.

The argument given above is somewhat supported by the results of surface area and total pore volume for the samples B_5 to B_9 prepared using various percentages of ammonium bicarbonate with CrO_3 allowing the formation of ammonium dichromate and chromate *in situ*. As can be seen from Table 2, sample B_2 shows maximum surface area and highest total pore volume in which case ammonium dichromate has been formed *in situ* during kneading by adding of 10 per cent ammonium bicarbonate. This trend is also maintained in sample B_1 where ammonium chromate has been formed and the favourable effects towards physical parameters are apparent when compared with the surface area and pore volume of B_3 where ammonium chromate has been used as such. These results thus indicate that if the chromium salt is prepared *in situ* during kneading, it helps to enhance the surface area and other parameters. This finding may be explained if the evolutions of CO_2 during kneading is taken into account, which gives the catalytic mass a honeycomb structure. However, the presence of free excess of ammonium bicarbonate in samples B_8 and B_9 does not help further improvement of their physical parameters.

Activity Results: The activities, in general, can be related to the mode of thermal decomposition of the chromium salts used. The sample B_4 appears to show the highest activity at lower temperatures and the activities of B_2 and B_3 are more than that of B_1. The samples B_5 to B_9 show fairly good activity and there is a diminishing trend with further addition of ammonium bicarbonate beyond 20 per cent which is the amount required to convert completely chromic acid into ammnium chromate. B_6 and B_7 show slightly better activity when compared with B_2 and B_3 respectively.

In case of B_4, the formation of γ-Fe_2O_3 is helpful for better activity due to the low activation energy of the latter[12,13]. In the cases of B_6 and B_7, a better activity is manifested due to the formation of dichromate and chromate *in situ* as well as for favourable structural parameters probably due to the finer distribution of chromia[3,14].

Conclusion

The findings, in general, tend to indicate that the promoter characteristics of chromia depend to some extent on the biography of its preparation. While chromate and dichromate are preferable to chromic acid to impart better promoter characteristics of the resulting chromia with regard to the activity although chromic acid appears to contribute towards robustness of the finished pellets. Though chromium acetate appears to help for better activity to catalytic mass, yet poor mechanical strength of the finished catalyst makes it quite unsuitable as a source of chromia. The *in situ* formation of chromate and dichromate appear to help to improve the activity and lower the apparent density of the catalytic component. The *in situ* incorporation may, therefore, be advisable for better dispersion of the promoter uniformly throughout the catalytic mass.

Acknowledgement

The authors are thankful to Shri B. Achari for his helpful suggestions regarding the above investigation.

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[Original mss. received on Aug. 15, 1973]

UDC 662.765: 543.862.2

A modified FIA method of hydrocarbon types analysis has been applied for the analysis of polycyclic aromatics in gas oil by using activated alumina as adsorbent.

Estimation of Poly-Cyclic Aromatics in Gas Oil

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The carcinogenic activity of some polycyclic aromatics has of late drawn considerable interest and progress has been reported in the detection and analysis of poly-aromatics in petroleum products and food materials with a view to control pollution. All poly-aromatics are, however, not carcinogenic. The important carcinogens[1] are benz-anthracene, dibenz-anthracene, denz-pyrene and their alkyl derivatives. Poly-aromatics are extracted by solvent extraction method, the usual solvents[2] being acetonitrile, nitromethane, dimethyl formamide, dimethyl sulphoxide, anhydrous phenol, etc. The extracted product is separated by column chromatography using silica gel or alumina as the adsorbent[3–6] and then the individual fractions are analysed by ultraviolet spectroscopy and spectrofluorometry[7–11]. Recently, mass spectroscopy and nuclear magnetic resonance spectroscopy[12] have also been applied successfully in the detection and estimation of individual poly-aromatics. However, all these methods are difficult, cumbersome and time-consuming. The present work describes a simple analytical technique for estimation of total poly-aromatics in gas oil and heavier petroleum distillate fraction by the application of the modified F.I.A. method for the analysis of hydrocarbon types in gas oil developed by the authors[13]. In the previous communication[13], the modifications of the standard ASTM method (D-1319-65) for application to gas oil include changes in the glass column, eluent composition and sample treatment. Incorporation of a longer separator section, increased viscosity of the eluent composition and dilution of viscous gas oil with a suitable diluent facilitated linear elution of the hydrocarbon types. However, using silica gel as the adsorbent in the modified column, the separation of poly-cyclic and mono-cyclic aromatics could not be achieved. As a consequence only the total aromatics value could be estimated. In the present work alumina, which is known to be an effective separator of aromatics, has been used in the modified column to separate poly-aromatics from mono-cyclic.

Experimental

The modified glass column[13] was packed with alumina (Brockmann Chromatographic grade mesh size 60-80 BSS) activated at 140°C for 4 hours and deactivated with 2 % water. A 0.2 ml sample of gas oil, diluted with equal volume of iso-octane to allow free flow of polyaromatics and heavy paraffins, was introduced with a syringe into the charger section of column. The remaining portion of the charger section was filled with the eluent mixture consisting of diethylene glycol and isopropanol (3:7 v/v). The use of a fluorescent indicator was not necessary. A suction of 1-2 psig was applied to the column from the bottom end. When the liquid front entered the analyser section, the vacuum was released and on attaining equilibrium, the fluorescent polyaromatics zone in ultraviolet light was measured and the percentage of polyaromatics calculated as below.

$$\text{Polyaromatics content volume } \% = 200\ \frac{\text{Length of Polyaromatics zone in mm.}}{\text{Total length of zone in mm.}}$$

Results and Discussion

The analysis of gas oil from Indian Oil Corporation's

This paper was presented at 61st Session of Indian Science Congress (1974) held at Nagpur.

Barauni Refinery for the polyaromatics has been carried out by the above technique. The results obtained are given below (Table 1).

TABLE 1—Analysis of Polyaromatics in Gas Oil Samples

Sl. No.	Sample	Boiling Range, °C	Composition, % v/v	
			Polyaromatics	Total Aromatics
1.	Gas oil	250-360	26.2	30
2.	Intermediate boiling range	250-270	15.2	20
3.	-do-	270-290	21.4	26
4.	-do-	290-320	28.8	32

Polyaromatics in gas oil are fluorescent in ultraviolet light and therefore self-indicating; hence addition of any other fluorescent dye is unnecessary. The other hydrocarbon types including monocyclic aromatics remain non-fluorescent resulting in a clear demarcation between poly-aromatics and other hydrocarbon types in the analyzer section of the glass column. The total aromatics value has been estimated by the modified FIA method[13].

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[Original mss. received on Dee. 3, 1973]

UDC 546.821: 620.193: 546.226.35: 546.19: 546.72

Weight-loss experiments have shown that trivalent arsenic and ferric iron are efficient inhibitors of corrosion of titanium in solutions of boiling dilute sulphuric acid (0.3, 0.6 and 1.2 g. H_2SO_4 per 100 ml.). There is a pronounced cathodic shift in potential of titanium in presence of these inhibitors in sulphuric acid solutions.

Effect of Trivalent Arsenic and Ferric Iron on the Corrosion of Titanium in Dilute Boiling Sulphuric Acid

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Introduction

Titanium as a material of construction in chemical industry has a great promise. A great advantage of using this material in chemical process equipment is that, unlike stainless steel, it is not susceptible to chloride stress-corrosion. As stainless steel is used in many chemical plants in contact with process streams containing inhibited boiling dilute sulphuric acid, its replacement by titanium would eliminate the risk of stress-corrosion that may be caused by small amounts of chlorides even in presence of inhibitors.

Although some work[1–16] has been carried out on corrosion of titanium in sulphuric acid, detailed studies on corrosion and inhibition of titanium in hot and boiling dilute sulphuric acid do not seem to have been made. Since such studies are important in fertilizer and allied industries, the present work was taken up.

Weight-loss experiments were carried out with titanium in boiling dilute sulphuric acid (0.3, 0.6 and 1.2 g. H_2SO_4 per 100 ml) in presence and absence of different quantities of trivalent arsenic and ferric iron as inhibitor. Electrode potential measurements were also done in the same solutions. The results are reported in this paper.

Experimental

For weight-loss experiments rectangular test coupons of 60 × 10 × 2 mm. size were sheared from commercially pure titanium (99.98 per cent purity) and a hole was drilled in each of them. The surface of the specimens were prepared on '600' grit wet silicon carbide paper. The coupons were degreased in boiling toluene and kept in desiccator for seven days before use. The coupons were suspended from glass hooks in the boiling solutions (*c.* 400 ml.) kept in 500 ml erlenmeyer flask fitted with a reflux condenser. The specimens were introduced into the solutions after they had been boiled for half an hour and were kept immersed for eight hours in the boiling solution and then taken out, washed with water, cleaned off adhering deposits degreased and weighed. The weight-losses were recorded in mg./sq. dm/day. Two or more experiments were carried out under each set of conditions and the average of the values taken.

For potential measurement a modified form of apparatus described by Streicher and similar to the one described in a previous communication[17] was used. Potential measurements were carried out by a potentiometer vs a saturated calomel electrode. All the potential values reported have been taken after 8 hours by which time the potential became steady. The potential values were reproducible within ± 10 mV and do not include corrections for junction potential and temperature.

In the experiments, sulphuric acid concentration was varied from 0.3 to 1.2 g/100 ml of acid. The arsenic concentration was varied from 0.005 to 5 g/100 ml and ferric iron from 2 to 25 ppm. Arsenic was added in the form of sodium arsenite and ferric iron as ferric chloride. All the chemicals used were of BDH analytical reagent grade.

Results and Discussion

In the uninhibited boiling sulphuric acid titanium corroded at a fast rate (Table 1). With the added arsenious oxide in a very low concentration of namely 0.005 g/100 ml in 0.3 g/100 ml acid, the corrosion rate was slightly more than in uninhibited acid and the corresponding potential was slightly more anodic. However, with further increase in the arsenic concentration to 0.01 g/100 ml and above, corrosion rates showed downward trend and the potential also less anodic. At 0.02 g/100 ml inhibitor concentration, the corrosion rate was reduced to 7.2 mdd and on further increasing the arsenic concentration, there was practically no corrosion. It is observed that the potential values become more noble in the presence of trivalent arsenic and there was an increasing shift in the cathodic direction with an increase in the arsenic concentration. With 5 g/100 ml arsenic there was a cathodic shift of 632 mV in the potential of titanium.

At 0.6 and 1.2 g/100 ml acid concentration with the addition of increasing arsenic, similar behaviour was observed as with 0.3 g/100 ml. At arsenious oxide concentration of 0.02 g/100 ml higher corrosion rates were observed than in uninhibited acid in both the acid concentrations and the potential values also more anodic. However, with further increase in the arsenic concentration the corrosion rates gradually dropped to low values. Very low values of corrosion rates were observed at arsenious oxide concentration of 0.06 g/100 ml in 0.6 g/100 ml acid and 0.15 g/100 ml in 1.2 g/100 ml acid. The potential values in both the acid concentrations showed cathodic shift with a corresponding increase in the inhibitor concentration.

From the potential data it is apparent that in each acid concentration a cathodic or anodic shift in potential is observed with the corresponding decrease or increase in the corrosion rate. Moreover the potential of titanium must reach a certain value in the anodic direction before appreciable corrosion sets in. This value seems to be more negative than —595 mV vs SCE in the present series of investigations. The high values of cathodic shift in the presence of trivalent arsenic indicates that it is behaving as an anodic inhibitor. This inhibitor was commonly supposed to be cathodic[18,19] one in acid solution. However, in an earlier publication[17] from this laboratory it has been shown that trivalent arsenic behaves as an anodic inhibitor when it inhibits corrosion of stainless steel in sulphuric acid solution. It was suggested that the inhibitor functions by forming a chemisorptive dative bond with the metal.

It is likely that the same mechanism also operates in the present case, i.e. the trivalent arsenic forms a chemisorptive bond at the anodic sites of titanium by donation of pair of electrons. This would explain the inhibition of corrosion and also the cathodic shift in potential due to reduction in effective anodic sites on the metal. The increased corrosion rates at low inhibitor concentration would be in line with the general effect of anodic inhibitors which when present in insufficient amounts result in a greater corrosion of the metal than in the case when no inhibitor is present[18].

Table 2 shows the effect of ferric iron on the corrosion rate of titanium in sulphuric acid. In 0.3 g/100 ml acid the corrosion rate was reduced to a very low value, viz. 7.2 mdd at a ferric iron concentration of 4 ppm. With increase in inhibitor concentration to more than 4 ppm

TABLE 1—EFFECT OF TRIVALENT ARSENIC AS INHIBITOR ON THE CORROSION OF TITANIUM IN BOILING DILUTE SULPHURIC ACID

Sl. No.	Concentration of As_2O_3, g./100 ml.	0.3 g./100 ml. H_2SO_4		0.6 g./100 ml. H_2SO_4		1.2 g./100 ml. H_2SO_4	
		Corrosion rate, mg./sq. dm/day	Potential vs SCE, mV	Corrosion rate, mg./sq. dm/day	Potential vs SCE, mV	Corrosion rate, mg./sq. dm/day	Potential vs SCE, mV
1.	None	613.0	−753	1083.0	−695	1776.0	−668
2.	0.005	651.0	−766	1092.0	−711	—	—
3.	0.01	612.0	−726	1091.0	−711	1783.0	−696
4.	0.02	7.2	−317	1204.0	−738	2039.0	−711
5.	0.04	7.1	−295	1024.0	−647	1843.0	−680
6.	0.06	5.3	−296	6.0	−595	1766.0	−658
7.	0.08	5.0	−297	5.8	−558	1460.0	−653
8.	0.10	3.5	−290	3.6	−250	1178.0	−627
9.	0.15	3.4	−288	3.6	−262	4.0	−554
10.	0.30	No Corrosion	−224	—	—	—	—
11.	1.00	,,	−135	No Corrosion	−172	3.5	−420
12.	2.00	,,	−130	,,	—	No Corrosion	−146
13.	5.00	,,	−121	,,	—	,,	—

TABLE 2—CORROSION AND INHIBITION OF TITANIUM IN BOILING DILUTE SULPHURIC ACID IN PRESENCE AND ABSENCE OF FERRIC IRON

Sl. No.	Concentration of Ferric iron, ppm	0.3 g./100 ml. H_2SO_4		0.6 g./100 ml. H_2SO_4		1.2 g./100 ml. H_2SO_4	
		Corrosion rate, mg./sq. dm/day	Potential vs SCE, mV	Corrosion rate, mg./sq. dm/day	Potential vs SCE, mV	Corrosion rate, mg./sq. dm/day	Potential vs SCE, mV
1.	None	613.0	−753	1083.0	−695	1776.0	−668
2.	2	308.0	−712	538.0	−745	1441.0	−726
3.	4	7.20	−355	8.90	−320	8.90	−312
4.	6	5.0	+92	6.10	+466	6.00	−440
5.	8	5.0	+307	—	—	—	—
6.	10	5.20	+534	—	—	—	—
7.	15	4.50	+557	—	—	—	—
8.	20	3.60	+600	3.60	+600	3.60	+600
9.	25	3.60	+605	—	—	—	—

further reduction in corrosion rate was not appreciable. The potential values become more noble in the presence of ferric iron and there is an increasing shift in the cathodic direction with an increase in the inhibitor concentration. At inhbitor concentration of 20 ppm, the total cathodic shift was 1353 mV vs SCE.

Similar behaviour of ferric iron was observed at 0.6 g. and 1.2 g./100 ml acid concentrations. From the potential data in the three acid concentrations, it is apparent that a cathodic shift is observed with the corresponding decrease in the corrosion rate with increased amounts of inhibitor concentration. The likely mechanism in this case would be thus similar to that of arsenic in the formation of a strong chemisorptive bond at the anodic sites of titanium with satisfaction of surface valencies. A similar mechanism has been suggested by Uhlig and Cobb[20] who have also shown that ferric iron inhibits corrosion of titanium in sulphuric acid.

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[Original mss. received on April 20, 1973]

UDC 141.24: 620.193: 631.8

The electrode potential behaviour of mild steel in cooling waters in presence of orthophosphate, chromate and polyphosphate has been studied. A pronounced cathodic shift in potential was observed in the presence of these inhibitors.

Effect of Orthophosphate, Chromate and Polyphosphate on the Electrode Potential of Mild Steel

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For the reduction of corrosion by cooling waters, inhibitors, like chromates, phosphates, nitrites and alkalies, have been used. Extensive work has been done in this laboratory[1–7] to find out suitable inhibitor combinations for minimizing corrosion by cooling waters. In a previous communication[7], studies on the effect of orthophosphate, chromate and polyphosphate on the corrosion behaviour of mild steel, brass and admiralty has been reported. The present investigations were made to study the electrode potential behaviour of mild steel in the above inhibitor combination.

Experimental

Rectangular test coupons of 6.2 × 10 × 2 mm. size were cut from mild steel sheet which corresponded to IRSM 16/49 manufactured by M/s Tata Iron and Steel Co. Ltd. For surface preparation the coupons were finally finished on '0' emery paper and degreased in boiling toluene.

The corrosion experiments were performed in a 2 litre Erlenmeyer flask. The inlet and outlet of the water to the flask were connected to a 20 litre reservoir, whose water was continuously circulated and aerated as described in a previous communication[7] and maintained at 52 ± 1°C. For weight-loss experiments, the coupons were kept completely immersed in water for 8 hr and the weight-loss was recorded as mg./sq. dm/day.

For potential measurements, the coupons were connected to a rod of the same composition. The experimental set-up was similar to the one described earlier[8]. The potential measurements were carried out using an external galvanometer and recorded after 8 hrs by which time the potential became steady. The values were reproducible within ± 10 mV.

For all experiments, synthetic cooling water as given in Table 1 was prepared by dissolving A.R. grade chemicals in distilled water. This was necessary as potential values were very erratic in cooling tower waters from the plant.

TABLE 1—Analysis of Water

Ingredient	Concentration, ppm
'M' Alkalinity as $CaCO_3$	8
Chloride as Cl	35.0
Sulphate as SO_4	48.0
Nitrogen (Ammonical)	2.0
Nitrogen (Nitrate)	28.0
Calcium	60.0
T. D. S.	305.0

Results and Discussion

The results (Table 2) show that in uninhibited water the corrosion rate of mild steel was 466.6 mdd. With the addition of 10 and 20 ppm polyphosphate along with 40 ppm chromate, the corrosion rates were reduced to low values but the appearance of the coupons were clean only at 20 ppm polyphosphate level. The effect of

TABLE 2—EFFECT OF ORTHOPHOSPHATE, CHROMATE AND POLYPHOSPHATE ON THE ELECTRODE POTENTIAL AND CORROSION RATE OF MILD STEEL IN COOLING WATER

(Vol. of solution 20 litres; Rate of circulation — 2.61 gal/min; Temperature 52± 1°C; Duration of experiment 8 hr)

Sl. No.	Inhibitor Concentration, ppm			pH	Potential, mV	Corrosion Rate, mg./sq. dm/day	Remark
	Orthophosphate as PO_4	Dichromate as CrO_4	Polyphosphate as PO_4				
1.	—	—	—	7.10	−770	466.6	General corrosion
2.	—	40	—	6.10	−640	49.5	Pitting occurs
3.	—	40	10	6.15	−620	25.2	Slight pitting occurs
4.	—	40	20	6.15	−610	24.0	Coupon clean
5.	1000	—	—	7.90	−466	49.3	Slight pitting occurs
6.	1000	40	—	7.80	−437	10.6	Coupon clean
7.	1000	40	10	—	−326	5.90	
8.	1000	40	20	7.80	−317	4.5	
9.	500	—	—	7.50	−549	59.8	Slight pitting occurs
10.	500	40	—	7.20	−500	13.80	Coupon clean
11.	500	40	10	7.5	−500	7.9	
12.	500	40	20	7.45	−461	6.5	
13.	250	—	—	7.2	−580	96.2	Pitting occurs
14.	250	40	—	6.9	−542	19.6	Coupon clean
15.	250	40	10	7.35	−520	11.9	
16.	250	40	20	7.35	−506	9.2	
17.	150	—	—	6.9	−610	107.9	Pitting occurs
18.	150	40	—	6.85	−590	22.5	Slight etching
19.	150	40	10	7.1	−570	12.8	Coupon clean
20.	150	40	20	7.0	−555	12.3	
21.	100	—	—	6.5	−616	124.2	Pitting occurs
22.	100	40	—	6.85	−605	25.6	Slight pitting occurs
23.	100	40	10	7.0	−590	14.9	Coupon clean
24.	100	40	20	6.85	−582	14.4	
25.	50	—	—	6.8	−625	181.9	Pitting occurs
26.	50	40	—	—	−615	35.5	
27.	50	40	10	6.85	−605	18.0	Slight pitting
28.	50	40	20	6.7	−600	—	Slight etching

increasing orthophosphate content from 50 to 1000 ppm reduced the corrosion rate to low values. With the addition of 40 ppm chromate along with orthophosphates, the corrosion rates were further lowered and coupons appeared clean. With the addition of 10 and 20 ppm of polyphosphate along with orthophosphate and chromate the inhibitive action of the combination increased.

The potential values in the presence of orthophosphate became less anodic and there was an increasing shift in the cathodic direction with the increase in the concentration of orthophosphate. The total cathodic shift observed with 1000 ppm orthophosphate was 304 mV vs saturated calomel electrode. With the addition of 40 ppm chromate along with orthophosphate, the cathodic shift was more marked than with orthophosphate alone. In the presence of 10 and 20 ppm polyphosphate along with chromate and othrophosphate, the potential becomes more noble and there was a marked cathodic shift with the increase in the concentration of polyphosphate. In the presence of chromate-polyphosphate mixture alone, the cathodic shift of potential was well marked but to a lesser extent than in the presence of orthophosphate chromate and polyphosphate mixture.

The effective inhibition of corrosion by the inhibitor combination coupled with pronounced cathodic shift in the potential suggests a strong chemisorption of the inhibitors on the anodic sites of the mild steel. This is in line with the views expressed by several investigators on the action of other effective inhibitors.

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[Original mss. received on Dec. 10, 1973]

UDC 66.045.5: 546.212: 543: 549.731.15

A method has been developed for the estimation of chromate in cooling waters containing free chlorine and nitrite. It consists in separating the chromate by precipitation with barium acetate and estimating it iodometrically in the precipitate.

A Method for the Estimation of Chromate in Cooling Waters Containing Free Chlorine and Nitrite

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Chromate or chromate-polyphosphate mixtures are commonly used in cooling waters for the prevention of corrosion and scale formation. Chromate and free chlorine alone or in combination are suitable for the control of bacterial activity in cooling tower waters. Due to the presence of free chlorine, nitrite and organic matter in the cooling tower waters, usual iodometric method for the estimation of chromate in these waters is not satisfactory. In the present study, a method has been developed for accurate estimation of chromate in cooling tower waters in presence of free chlorine, nitrite and organic matter.

The method consists in separating the chromate present in water by precipitation with barium acetate and estimating it iodometrically in the precipitate.

Procedure

About 100 ml. of the chromate treated cooling water (containing up to about 500 ppm chromate) is taken and made neutral or weakly acidic with soda or acetic acid as the case may be. The solution is brought to boiling and 10 per cent solution of barium acetate is added drop-wise with constant stirring till it is present in slight excess. The solution is then placed on a water bath until the precipitate settles. Some more barium acetate is added to test the completeness of the precipitation. The precipitate is filtered under slight suction through a sintered or gooch crucible and washed three to four times with hot water. The precipitate is redissolved in minimum amount of 1:1 hydrochloric acid and chromate content is estimated iodometrically.

Discussion

In Table 1 are given the results of estimation of chromate by the standard method and the one evolved in the present study in absence of chlorine, nitrite and

TABLE 1—ESTIMATION OF CHROMATE IN ABSENCE OF FREE CHLORINE, NITRITE AND ORGANIC MATTER
(Each value represents average of six readings)

Chromate by the Usual Method (as mg. of CrO_4)	Chromate by the New Method (as mg. of CrO_4)
0.22	0.22
0.15	0.15
0.50	0.50

organic matter. There is complete agreement between the two sets of values.

In Table 2 are given the results of studies in which known amount of chromate was added to water containing free chlorine, nitrite and organic matter. There is complete agreement between the calculated and experimental values.

TABLE 2—ESTIMATION OF CHROMATE IN PRESENCE OF FREE CHLORINE, NITRITE AND ORGANIC MATTER
(Each value represents average of six readings)

Calculated Value of Chromate (as mg. of CrO_4)	Estimated Value of Chromate (as mg. of CrO_4)
0.22	0.22
0.15	0.15
0.10	0.10

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[Original mss. received on Dec. 10, 1973]

TECHNOLOGY

OFFER FOR EXCHANGE

This quarterly, TECHNOLOGY, is offered in exchange with other scientific and technical journals for mutual benefit. It is already being exchanged with about eighty journals—foreign and Indian. Editors of journals devoted to all branches of science and technology and particularly fertilizer technology, applied chemistry, chemical engineering, food technology, agronomy, agricultural chemistry, soil science, fuel technology, etc. may write to the Editor of TECHNOLOGY.

UDC 631.841.1 : 545.33 : 546.47

A well defined irreversible step having a half wave potential of – 1.18 V vs. SCE has been obtained for Zn^{2+} in ammoniacal 0.1 M ammonium sulphate at pH-9. This wave has been utilized for the estimation of Zinc in ammonium sulphate fertilizer without prior separation of impurities. The error in the estimation has been worked out to be within ± 1.0 per cent.

Polarographic Estimation of Zinc in Ammonium Sulphate Fertilizer

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Introduction

Zinc in the form of salts is mixed with fertilizers and applied to soil to overcome its deficiency. A knowledge of zinc content of the fertilizer is therefore helpful in assessing its correct dose to the soil. Polarographic methods for the estimation of zinc in nitrophosphate and superphosphate have been developed[1,2]. In this paper, a polarographic method has been worked out for the estimation of zinc in ammonium sulphate fertilizer.

Experimental

LP-60 polarograph with a capillary having characteristic $m^{2/3}t^{1/6}$—2.5 was used. The experimental techniques were the same as described earlier[1,2]. Ammoniacal ammonium sulphate (0.1 M) at pH 9 with gelatine as maximum suppressor was used to measure the pH of the experimental solutions. pH of the solution was adjusted by dilute ammonia solution. Stock solutions of zinc sulphate and ammonium sulphate were prepared by dissolving Analar grade chemicals in distilled water.

A calibration graph was prepared by taking 1.32 g. of ammonium sulphate and varying amounts of zinc solution in a series of beakers; pH of each solution was adjusted to 9 and the content of the beaker was transferred to a 100 ml. volumetric flask. After adding 1 ml. of 0.05 per cent gelatine solution, the solutions were made up to the mark. 20 ml. of aliquot was taken in the polarographic cell and a polarogram was recorded. From a series of polarograms, diffusion currents were calculated and plotted against the concentration of zinc (Fig. 1).

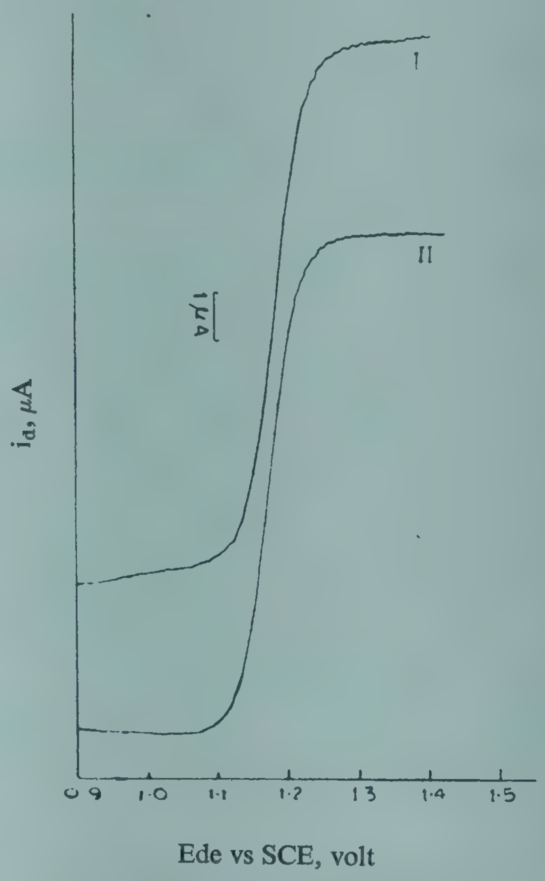

Fig. 1—Polarograms of Zn^{2+} in Ammoniacal Ammonium Sulphate

Curve I—Ammonium Sulphate (Analar)
Curve II—Ammonium Sulphate (Fertilizer)

TABLE 1—POLAROGRAPHIC ESTIMATION OF ZINC IN SYNTHETIC MIXTURES WITH KNOWN AMOUNTS OF AMMONIUM SULPHATE AND ZINC SULPHATE
(Sample taken = 1.32 g)

$(NH_4)_2SO_4$ Analar				$(NH_4)_2SO_4$ Fertilizer Grade			
Sample No.	Zn^{2+} added (mg)	Zn^{2+} found polarographically (mg)	% Recovery	Sample No.	Zn^{2+} added (mg)	Zn^{2+} found polarographically (mg)	% Error
AS_1	0.90	0.89	99.22	AF_1	1.30	1.30	0.00
AS_2	1.30	1.31	100.76	AF_2	2.10	2.11	+0.47
AS_3	1.70	1.70	100.00	AF_3	3.60	3.62	+0.55
AS_4	2.00	2.01	100.50	AF_4	3.00	2.99	−0.33
AS_5	2.80	2.81	100.35	AF_5	4.20	4.21	+0.23
AS_6	3.20	3.20	100.00	AF_6	2.65	2.66	+0.37
AS_7	3.70	3.701	100.03	AF_7	0.80	0.80	+0.00
AS_8	4.30	4.32	100.46	AF_8	4.40	4.42	+0.45

Samples of ammonium sulphate containing Zn^{2+} were prepared by throughly mixing a known amount of zinc sulphate to Analar and fertilizer grades ammonium sulphate. For the polarographic estimation of zinc in the fertilizer about 1.32 g. of the sample was taken in a 100 ml. beaker and dissolved in distilled water; pH was adjusted to 9. The content of the beaker was transferred to 100 ml volumetric flask, gelatine solution was added and the volume was made up to the mark. 20 ml of this aliquot was taken in the polarographic cell and a polarogram was recorded. The diffusion current was calculated and the concentration was found out from the calibration graph. The results of analysis are given in Table 1.

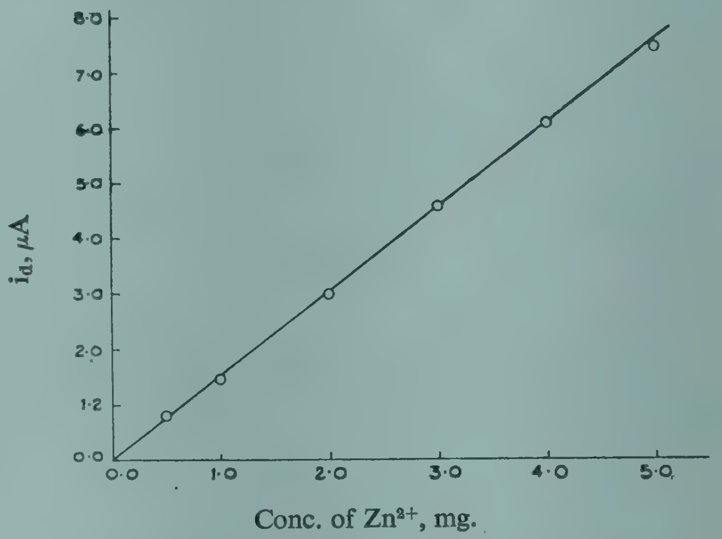

Fig. 2—Plot of Concentration of Zinc against i_d

Discussion

Ammoniacal media were found to be extremely useful for the determination of zinc in copper base[3,4] and lead base[5] alloys. In the present work, ammoniacal ammonium sulphate was used as base electrolyte for the reduction of zinc. The reduction wave, thus obtained, was utilized to determine micronutrient zinc in ammonium sulphate fertilizer.

A well-defined step having a half wave potential of −1.18 V vs SCE was obtained for Zn^{2+} in a base electrolyte solution composed of ammoniacal 0.1M ammonium sulphate+0.005% gelatine at pH 9. The slope of Ede vs log $\frac{i}{i_d-i}$ for the step was found to be 0.054, showing the system to be irreversible. The half wave potential of Zn^{2+} was found to shift to a more negative value with increasing pH and concentration of base electrolyte, confirming the complexing of zinc with ammonium sulphate. For analytical purpose, the pH of all experimental solutions were adjusted at 9 and the concentration of base electrolyte was fixed at 0.1 M ammonium sulphate. Well-defined polarograms were obtained of Zn^{2+} in Analar and fertilizer grades ammonium sulphate (Curves I & II, Fig. 2). The values of the various polarographic constants are given in Table 2. The similarity of

TABLE 2—VALUES OF $E_{1/2}$, id, SLOPE AND I FOR 1.0 mM Zn^{2+} WAVES IN ANALAR AND FERTILIZER GRADE AMMONIUM SULPHATE
(Base electrolyte: 0.10 M ammonium sulphate + 0.005 % gelatine)

Experimental Solution	$E_{1/2}$ vs SCE, volts	id, mA	Slope $\log \frac{i_d}{i_d-i}$	I
1. Ammonium Sulphate Analar (pH 9.0)	1.18	10.30	0.0545	4.12
2. Ammonium Sulphate Fertilizer Grade (pH 9.0)	1.18	10.25	0.0545	4.10

values for Zn^{2+} in the Analar and fertilizer grades ammonium sulphate confirmed that Zn^{2+} wave in fertilizer grade ammonium sulphate is unaffected by the impurities present in the fertilizer.

A linear plot of diffusion current against concentration of Zn^{2+} was obtained (Fig. 1), which was used as a standard for the estimation of Zn^{2+} in ammonium sulphate fertilizer. The suitability of the method was checked by adding a known amount of Zn^{2+} to ammonium sulphate (Analar grade). The zinc content of the sample was estimated polarographically and percentage recovery was calculated and found lying between 99 to 101 (Table 1). Ammonium sulphate fertilizer samples containing Zn^{2+} were also analyzed polarographically and the results are given in Table. 2. The percentage error has been worked out to be ±1.0 per cent. Further work on the application of the method to process liquors is in progress.

The present polarographic method provides a quick and accurate method for the estimation of zinc in ammonium sulphate fertilizer without removing any of the impurities.

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[Original mss. received on Oct. 21, 1973]

UDC 678.745.2:53:678.019.3

Chemical and physical resistance of the products from liquid epoxy resin cured with amido polyamine hardener, both developed in this laboratory, have been discussed. The properties have been compared with araldite, a trade name of a resin produced by CIBA (India) Ltd.

Chemical Resistance and Physical Properties of Diglycidyl Ether of Bisphenol—A Cured System with Amido Polyamine Hardener*, Part 2

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As reported earlier[1] epoxy resins based on bisphenol—A cured with amido-polyamine hardener[2] sets to a hard mass, depending on amine value, viscosity, time, temperature, etc., amine value being most important. The present communicaion deals with the properties of cured systems of liquid resin[3] with hardener[4], both developed in the laboratory. Studies have also been carried out with a renowned commercial epoxy resin[5] for comparison.

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*Indian Pat. Appl. No. 133003.

Experimental

Amido polyamine hardener[4] was used throughout the study. Like the other hardener[2], it is amber in colour, free-flowing but having approximately 300 amine value. Epoxy resins, like Araldite[5] and the resin[3], prepared in this laboratory having epoxide equivalent 180-194 and 250-280 respectively were used. The resin and hardener were mixed in 1:0.3, 1:0.4 and 1:0.5 ratios, which were cured at room temperature. Chemical resistance was determined after 15 days as in the earlier[1] case. The percentage of absorption of various chemicals was determined by dipping cured samples of resin and hardener (Tables 1 & 2). With many other chemicals only visual observation was made by dipping the sample in a particular chemical for 60 days (Table 3). Adhesive strength, shear strength and vicat softening point were also determined.

Adhesive Strength: This characteristic was determined

TABLE 1—PERCENTAGE OF CHEMICAL ABSORPTION OF CURED SAMPLES

Samples Tested In	Ratio of Resin[3] and Hardener[4]	Days						
		1st	2nd	3rd	4th	5th	6th	7th
30% Hydrochloric Acid	1:0.3	0.0231	0.0718	0.1052	0.1312	0.1635	0.1675	0.1718
	1:0.4	0.1054	0.1563	0.1901	0.2112	0.2321	0.2579	0.2830
	1:0.5	0.1859	0.2447	0.2901	0.3400	0.3751	0.4102	0.4357
20% Sodium Hydroxide	1:0.3	0.0558	0.0840	0.1072	0.1372	0.1521	0.1744	0.1930
	1:0.4	0.0717	0.1055	0.1263	0.1604	0.1782	0.1912	0.2060
	1:0.5	0.0569	0.0855	0.1099	0.1424	0.1604	0.1775	0.1988
5% Nitric Acid	1:0.3	0.1255	0.1883	0.2207	0.2553	0.2791	0.3010	0.3255
	1:0.4	0.1615	0.2102	0.2487	0.2858	0.3215	0.3551	0.3935
	1:0.5	0.2008	0.2520	0.3035	0.3588	0.3990	0.4462	0.4901
Distilled Water	1:0.3	0.1604	0.2056	0.2421	0.2796	0.3080	0.3378	0.3671
	1:0.4	0.1725	0.2200	0.2631	0.2948	0.3413	0.3847	0.4288
	1:0.5	0.2189	0.2794	0.3437	0.4146	0.4587	0.5056	0.5497
20% Solution of Urea	1:.03	0.0728	0.1053	0.1377	0.1649	0.1924	0.2250	0.2442
	1:0.4	0.1101	0.1457	0.1904	0.2303	0.2699	0.2924	0.3175
	1:0.5	0.1160	0.1614	0.1986	0.2413	0.2856	0.3145	0.3440
20% Solution of Ammonium Sulphate	1:0.3	0.0662	0.1168	0.1568	0.1902	0.2258	0.2562	0.2843
	1:0.4	0.0762	0.1303	0.1763	0.2187	0.2604	0.3026	0.3425
	1:0.5	0.0786	0.1371	0.1814	0.2321	0.2803	0.3131	0.3467
20% Solution of Double Salt	1:0.3	0.0630	0.1024	0.1300	0.1612	0.1970	0.2202	0.2370
	1:0.4	0.0680	0.1326	0.1608	0.1945	0.2291	0.2495	0.2672
	1:0.5	0.0985	0.1642	0.1970	0.2392	0.2831	0.3125	0.3488
Saturated Solution of Urea	1:0.3	0.0420	0.0846	0.1016	0.1354	0.1651	0.2012	0.2328
	1:0.4	0.0859	0.1084	0.1485	0.1794	0.2050	0.2402	0.2627
	1:0.5	0.0980	0.1195	0.1593	0.1872	0.2207	0.2508	0.2828
Saturated Solution of Ammonium Sulphate	1:0.3	0.0602	0.0871	0.1203	0.1536	0.1812	0.2116	0.2498
	1:0.4	0.0686	0.1114	0.1484	0.1814	0.2221	0.2680	0.3010
	1:0.5	0.0711	0.1179	0.1586	0.1992	0.2391	0.2805	0.3130
Saturated Solution of Double Salt	1:0.3	0.0300	0.0640	0.1023	0.1294	0.1652	0.2004	0.2325
	1:0.4	0.0562	0.0924	0.1285	0.1526	0.1820	0.2224	0.2550
	1:0.5	0.0774	0.1018	0.1425	0.1792	0.2108	0.2403	0.2710

TABLE 2—Percentage of Chemical Absorption of (Araldite Resin[5] and Hardener[4]) Cured Samples

Samples Tested In	Resin: Hardener	Days						
		1st	2nd	3rd	4th	5th	6th	7th
30% Hydrochloric Acid	1:0.3	0.2387	0.2813	0.3283	0.3581	0.3922	0.4305	0.4561
	1:0.4	0.2548	0.3178	0.3601	0.3912	0.4237	0.4535	0.4831
	1:0.5	0.2848	0.3505	0.3942	0.4358	0.4733	0.4984	0.5248
20% Sodium Hydroxide	1:0.3	0.1046	0.1255	0.1464	0.1692	0.1925	0.2134	0.2218
	1:0.4	0.1278	0.1619	0.1966	0.2287	0.2599	0.2897	0.3108
	1:0.5	0.1267	0.1690	0.2112	0.2508	0.2873	0.3167	0.3294
5% Nitric Acid	1:0.3	0.2544	0.3350	0.4028	0.4519	0.4962	0.5174	0.5343
	1:0.4	0.3070	0.3750	0.4434	0.4925	0.5458	0.5797	0.6054
	1:0.5	0.3419	0.4046	0.4631	0.5101	0.5535	0.5878	0.6176
Distilled Water	1:0.3	0.2704	0.3348	0.3606	0.3891	0.4034	0.4421	0.4722
	1:0.4	0.3114	0.3892	0.4541	0.5150	0.5838	0.6357	0.6747
	1:0.5	0.3496	0.4261	0.4957	0.5616	0.6305	0.6956	0.7739
20% Solution of Urea	1:0.3	0.1752	0.2813	0.3228	0.3562	0.3918	0.4196	0.4380
	1:0.4	0.1932	0.2918	0.3369	0.3702	0.4042	0.4267	0.4491
	1:0.5	0.2029	0.3019	0.3538	0.3921	0.4292	0.4579	0.4718
20% Solution of Ammonium Sulphate	1:0.3	0.1756	0.2633	0.3335	0.3811	0.4300	0.4608	0.4740
	1:0.4	0.2217	0.2852	0.3566	0.4057	0.4545	0.4857	0.5081
	1:0.5	0.2244	0.2868	0.3532	0.4222	0.4773	0.5012	9.5250
20% Solution of Double Salt	1:0.3	0.1595	0.2284	0.2844	0.3418	0.3966	0.4310	0.4568
	1:0.4	0.1621	0.2351	0.3002	0.3559	0.4178	0.4571	0.4874
	1:0.5	0.1942	0.2560	0.3133	0.3751	0.4413	0.4721	0.4943
Satutated Solution of Urea	1:0.3	0.1064	0.1595	0.1861	0.2087	0.2286	0.2526	0.2704
	1:0.4	0.1317	0.1844	0.2152	0.2352	0.2575	0.2810	0.2980
	1:0.5	0.1430	0.1967	0.2280	0.2526	0.2782	0.3040	0.3218
Saturated Solution of Ammonium Sulphate	1:0.3	0.1285	0.1970	0.2116	0.2335	0.2512	0.2748	0.2880
	1:0.4	0.1323	0.2116	0.2294	0.2527	0.2742	0.2955	0.3220
	1:0.5	0.1683	0.2274	0.2547	0.2825	0.3080	0.3365	0.3547
Saturated Solution of Double Salt	1:0.3	0.1172	0.1738	0.1955	0.2058	0.2164	0.2259	0.2346
	1:0.4	0.1381	0.1943	0.2246	0.2404	0.2592	0.2764	0.2894
	1:0.5	0.1454	0.2113	0.2423	0.2538	0.2752	0.2864	0.2995

by a Hounsfield tensometer. Applying the mixture of resin and hardener on both sides of the mild steel test pieces (Fig. 1) and joining them together, pressure was applied uniformly to maintain glue-line thickness of about 0.10 mm. The joined pieces were firmly gripped after 7 days of application of the adhesive mixture and stress was applied through a handle and the load required to separate the pieces was noted. Observing the test pieces, failure was found to be due to adhesion while cohesion remains intact. For each ratio, more than six readings were taken and the average value tabulated (Table 4).

Shear Strength: Using the above equipment two mild steel test pieces (Fig. 2) were joined by the mixture of resin and hardener in different ratio and the thickness of glue-line was maintained uniformly at about 0.15 mm for all the systems by applying equal pressure. The testing for shear strength was carried out after 7 days and the averages of minimum six readings were tabulated (Table 4).

TABLE 3—CHEMICAL RESISTANCE PROPERTIES OF CURED EPOXY SYSTEMS

Sl. No.	2 Months Immersion at Room Temp. (25-28°C)	Concentration, %	Resin[3] and Hardener[4]	Araldite GY-250[5] and Hardener[4]
1.	Acetic Acid	10	Resistant	Resistant
2.	Acetic Acid	30	Partial resistant	Partial resistant
3.	Acetic Acid	100	Non-resistant	Non-resistant
4.	Nitric Acid	10	Resistant	Resistant
5.	Phosphoric Acid	10	Resistant	Resistant
6.	Phosphoric Acid	30	Resistant	Resistant
7.	Sulphuric Acid	10	Resistant	Resistant
8.	Sulphuric Acid	30	Resistant	Resistant
9.	Hydrochloric Acid	30	Resistant	Resistant
10.	Deionized Water	—	Resistant	Resistant
11.	Sodium Hydroxide	20	Resistant	Resistant
12.	Benzene	100	Non-resistant	Non-resistant
13.	Ethyl Alcohol	40	Resistant	Resistant
14.	Ethyl Alcohol	96	Partial resistant	Partial resistant
15.	Ethyl Methyl Ketone	100	Non-resistant	Non-resistant
16.	Toluene	100	Non-resistant	Non-resistant
17.	Aniline	100	Non-resistant	Non-resistant
18.	Acetone	10	Resistant	Resistant
19.	Acetone	30	Resistant	Resistant
20.	Acetone	100	Non-resistant	Non-resistant
21.	Kerosene Oil	—	Resistant	Resistant
22.	Naphtha	—	Resistant	Resistant

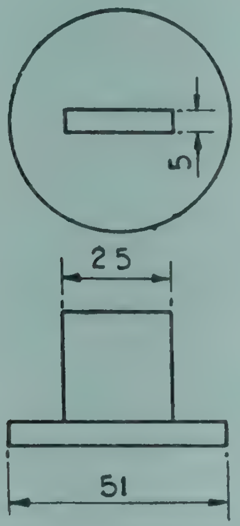

Fig. 1—Adhesive Test Piece

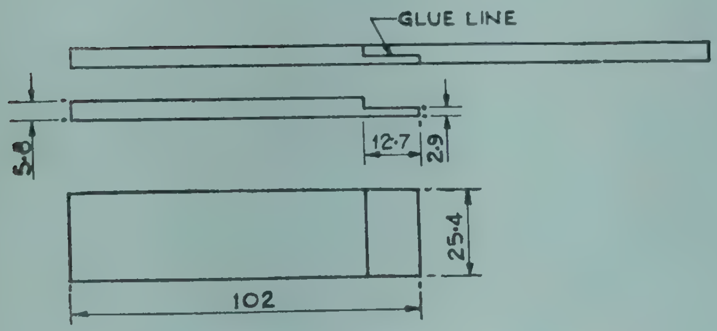

Fig. 2—Shear Test Piece

TABLE 4—PHYSICAL PROPERTIES OF CURED EPOXY SYSTEMS

Experiment	Mixing Ratio of Resin and Hardener	Curing Time	Experimental Result, psi	
			Resin[3] and Hardener[4]	Araldite GY-250[5] and Hardener
Adhesive strength	1: 0.3	7 days	330	345
	1: 0.4		230	210
	1: 0.5		230	210
Shear strength	1: 0.3	7 days	1700	750
	1: 0.4		1200	1150
	1: 0.5		1050	1225

Vicat Softening Point: Using Vicat testing apparatus*, this softening point of the mould pieces was determined by keeping them in the apparatus after 15 days of preparation over which a needle having 1 sq. mm of circular cross section was suspended. Applying 5.00 Kp load vertically over the needle uniform heating was allowed and the temperature was noted when the needle penetrated 1 mm into the sample and the average of three readings tabulated (Table 5).

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*The apparatus, named after Vicat of German Democratic Republic, determines dimensional stability under heat.

TABLE 5—VICAT SOFTENING POINT OF CURED EPOXY SYSTEMS

Mixing Ratio of Resin and Hardener	Curing Time	Vicat Softening Point, °C	
		Resin[3] and Hardener[4]	Araldite GY-250[5] and Hardener[4]
1 : 0.3	15 days	60°	50°
1 : 0.4		65°	59°
1 : 0.5		68°	67°

Discussion

The moulds were made by mixing hardener and resin in ratio 0.3, 0.4 and 0.5 to 1. Those prepared in the ratio 0.3:1 were soft after 24 hr. However, for absorption of chemicals, samples of $1' \times \frac{1}{2}'' \times \frac{1}{4}''$ were cut and the absorption noted. From Tables 1 and 2, it is evident that the percentage of absorption is lowest in all the the cases with 0.3 hardener, and with resin[3] absorption is less as compared with Araldite GY-250[5] under similar conditions. The percentage of absorption in almost all cases with resin[3] was found to be in the following increasing order $0.3 < 0.4 < 0.5$, except with caustic soda (Table 1) where the percentage of absorption is in the order of $0.3 < 0.5 < 0.4$.

The chemical resistance observed visually with 15 chemicals at different concentrations was found to be same for both the resins (Table 5). 'Resistant' denotes no chipping, swelling, or deformations of the mould while 'partially resistant' indicates some softening after 20 days and 'non-resistant' indicates complete failure of the sample within 3-4 days. The observations were carried with the samples at all the ratios yielding similar results.

The results (Table 4) indicate that maximum adhesive strength is obtained when 0.3 of hardener was mixed with one of both the types of resin. With 0.4 hardener to one resin ratio, the adhesive strength decreased, remaining unchanged at 0.5 hardener ratio. However, with Araldite GY-250[5] and resin[3], the adhesive strength was almost the same. The shear strength in case of GY-250[5] increased with increase in the ratio of hardener whereas reverse was the case with the resin prepared in this laboratory with similar amount of hardener.

Table 5 indicating vicat softening point for the cured samples at 0.3, 0.4 and 0.5 ratio of hardener with 1 of Araldite GY-250 and our resin respectively. The temperatures indicate penetration of 1 mm. length of the needle. The vicat softening point increases with increase in the ratio of hardener with both the resins; with our resin this point is high.

From the above discussion, it can be concluded that (i) 1:0.3 mixture of resin and hardener is the best ratio for the properties mentioned except vicat temperature, provided the end use is made after 10-15 days; (ii) for immediate use, i.e. within 24 hr, 1:0.5 ratio would be better; and (iii) at higher temperatures 0.5 ratio of hardener gives better result as compared to 0.3.

Acknowledgement

The authors are thankful to the General Manager, Planning and Development Division, FCI Ltd. for his interest and encouragement in this work.

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[Original mss. received on March 18, 1973]

UDC 621.374.4: 621.385.2

Wideband frequency doubling by utilizing the non-linear forward character of diodes is discussed. A circuit achieving a large band width using even grossly mismatched components is described.

Wideband Frequency Doubler

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Frequency doublers are widely used in wave form synthesis, telecommunication and instrument design[1]. While procedure is standardized for fixed frequency applications, considerable interest still exists in wide band frequency doublers. These, in general, employ squaring circuits, which are costly and complicated[2] to make. The advantage is often taken of the non-linearity of the voltage current characteristics of a diode or other devices[3], and by adding the outputs of two carefully matched devices driven in opposite phase, an effective squaring is obtained. Recently, Subbarao[4] has developed a frequency doubler circuit using a pair of quasi-matched MOSFET's.

A much simpler method of frequency doubling over a wide band is described here. It has the advantage of employing ordinary components which need not be matched. The non-linear elements employed here are two point contact diodes.

Theoretical

The current-voltage relationship of a forward biased diode can be expressed as a power series.

$$I=I_0+aE+bE^2+cE^3+ \qquad (1)$$

where I is the forward current, I_0 is a constant related to the threshold conduction potential, E is the input voltage and a, b and c are constants. For ordinary diodes, $a \gg b \gg c$, so that for small inputs, the series can be terminated at the quadratic term without incurring appreciable error. If the applied voltage E is expressed as the sum of a constant forward bias E_0 and a sinusoidal part, e sinpt, then

$$\begin{aligned} I &= I_0+a\,(E_0+e\sin pt)+b\,(E_0+e\sin pt)^2 \\ &= (I_0+aE_0+bE_0^2)+(a+2bE_0)\,e\sin pt+be^2\sin^2 pt \\ &= A+B\sin pt+C\sin^2 pt \qquad (2) \end{aligned}$$

where the coefficients A, B and C have been substituted to simplify the expression.

Considering a second diode with identical characteristics, under identical conditions, except for the phase of the input signal, which is now assumed to be opposite to the first case,

$$I'=A-B\sin pt+C\sin^2 pt \qquad (3)$$

Adding (2) and (3)

$$\begin{aligned} I+I' &= 2(A+C\sin^2 pt) \\ &= (2A+C)-C\cos^2 pt \qquad (4) \end{aligned}$$

The quantity in parentheses represent a DC term which can be blocked out by a condenser, leaving in the output an AC term at double the input frequency. The circuit (Fig. 1) suggests itself from the above. But the

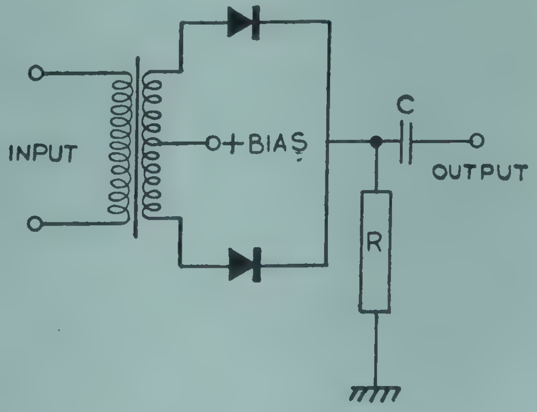

Fig. 1—Circuit

requirements of exact matching of the diodes and tapping at the exact centre of the transformer secondary are difficult to meet in practice. The output here will always contain a component at the input frequency.

It is now going to be shown that there is no necessity for such exactitude, if one of the diode input amplitudes can be adjusted properly. As before, the expressions for the two diode currents can be written as

$$\begin{aligned} I &= A + B\ \sin pt + C\ \sin^2 pt \\ I' &= A' - B'\ \sin pt + C'\ \sin^2 pt \end{aligned} \qquad (5)$$

$$\begin{aligned} \therefore\ I + I' &= A + A' + (B - B')\ \sin pt + (C + C')\ \sin^2 pt \\ &= A + A' + \tfrac{1}{2}(C + C') + (B - B')\ \sin pt \\ &\quad - \tfrac{1}{2}(C + C')\ \cos^2 pt \end{aligned} \qquad (6)$$

This can be brought to the form (4), if $B = B'$. It implies that

$$\frac{e}{e'} = \frac{a' + 2b'E_0}{a + 2bE_0} \qquad (7)$$

where the explicit forms for B and B′ have been written out, e and e′ being the amplitudes of the AC inputs. Now, in the general case, there may be a functional dependence of the bias voltage on the signal amplitude through the use of biasing elements, so $E_0 = f(e, e')$ and $E'_0 = f'(e, e')$. However, remembering $a \gg b$, the effect of variation of the bias voltages with the input amplitudes will be small, and it will be always possible to balance out B and B′ by choosing proper values of e and e′.

Experimental and Results

A practical form of a circuit employing the principle outlined above is shown in Fig. 2. The two 1N38 diodes used as the non-linear elements are deliberately chosen to have widely different forward characteristics, as shown in Fig. 3. The AC inputs in opposite phases are provided by the transistor paraphase amplifier. The e/e′ ratio required for cancelling the input frequency component according to equation (7) is achieved by adjusting the collector load R (Fig. 2). The DC bias voltages E_0 and E'_0 are optimized by adjusting the DC return resistor R_1. Frequency doubled output is taken through the capacitor C.

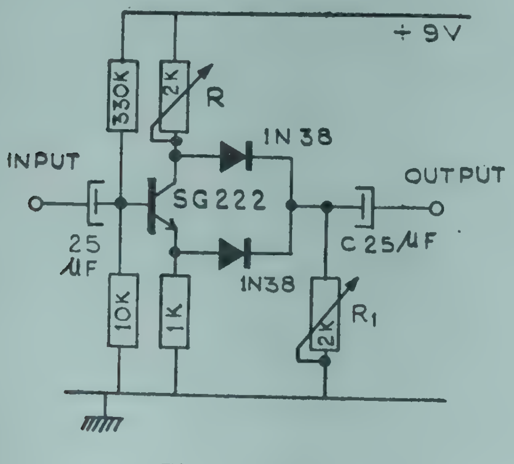

Fig. 2—Circuit

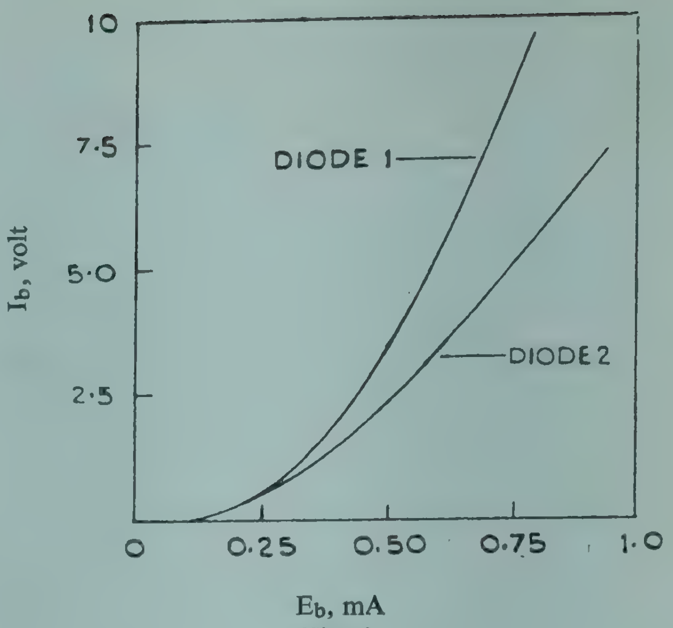

Fig. 3

With the circuit parameters shown, distortionless frequency doubling has been obtained over the frequency range 20 Hz. to 200 kHz. The limitation in the bandwidth was due to the deliberate mismatch of the diodes. Bandwidth can be greatly enlarged by using better matched components.

At very high frequencies, a transistor phase splitter stage may prove ineffective because of the junction capacitances. UHF tubes and diodes should be used for video doublers.

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Superintendent, Physical Wing, for his kind interest in the work, and to Dr. P. K. Ghosh for helpful suggestions.

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[Original mss. received on June 15, 1973]

UDC 547.652.1: 544.66: 546.56

Trace amount of copper in naphtha samples has been estimated by using aqueous standards with the help of a λ-shaped double capillary aspiration system.[1] A method developed earlier[2] has been adopted for the present work. Copper was found absent in three out of nine samples taken up for the present investigation.

Use of Aqueous Standards for the Estimation of Trace Amount of Copper in Naphtha by Atomic Absorption Spectrophotometry

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Introduction

In the estimation of trace elements in petroleum products, standard solutions for the elements of interest are generally prepared by dissolving organo-metallic compounds in a pure organic solvent. Using such standards, Barras[3] estimated traces of copper, iron and nickel in crude oil, while some other workers[4–6] determined some elements in the lubricating oils. Moore *et al*[7] estimated copper, lead and nickel in gasoline. Nickel was also determined in the cracking feedstock by Kerber[8] and Trent and Slavin[9]. The organo-metallic standards are not very stable, moreover only a few foreign firms supply them.

In the absence of the above standards, the petroleum samples can be analysed by ashing procedure which is lengthy and troublesome. In this laboratory, naphtha (an important feedstock for fertilizer production) samples were often analysed by this method for the impurities, viz. iron, copper, vanadium and lead. The ash content of the samples was very small, moreover, Horeczy *et al*[10] showed that there is a loss of ash in dry ashing and so an accurate analysis was difficult.

To overcome the above difficulties, a method was developed[2] in this laboratory, wherein aqueous standards were used for the estimation of iron in naphtha by atomic absorption spectrophotometry (AAS) using a λ-shaped double capillary aspiration system (DCS)[1]. It was observed that when two immiscible liquids, such as naphtha and water, are aspirated through the two lower capillaries of DCS, they get forcibly mixed (to form a homogeneous suspension) at the junction and behave in the flame as if they are miscible ones. Further, the flow-rate of the liquid through one lower capillary is proportional to the viscosity of the liquid through the other capillary and as such a viscosity correction has to be applied. A similar method has been adopted in the present work for the estimation of trace amount of copper in some naphtha samples using aqueous standards. The apparent copper contents determined against aqueous standards were multiplied by the viscosity of the working naphtha samples to get the actual copper values.

Experimental

Equipment: A Perkin-Elmer model 303 atomic absorption spectrophotometer equipped with an air-acetylene burner head and a copper hollow cathode lamp was used. Instead of the single capillary (for aspiration of samples) a DCS (1:1) made as earlier[1] was used.

Procedure: Nine naphtha samples (supplied by Barauni oil refinery) were collected from different batches used in the Sindri fertilizer factory. The samples were diluted × 5 with methyl iso-butyl ketone (MIBK). From 1 per cent Harleco standard solution of copper, three copper standards (0.025, 0.05 and 0.10μg/ml respectively) were prepared by dilution with distilled water. MIBK itself was used as a blank. The viscosity of the diluted naphtha samples, measured by an oswald viscometer was found to be 0.59 poise in each case.

The experimental conditions for copper were set as given in analytical methods[11]. To compensate for the enrichment of the flame due to the organic liquid, acetylene flow was reduced until the flame just lifted off the burner. The zero of the instrument (using a scale expansion of × 10) was adjusted by aspirating MIBK (blank) through one of the lower capillaries of DCS and water through the other. While continuously aspirating MIBK through one capillary, the three aqueous copper standards (prepared above) were aspirated through the other capillary one after the other and the corresponding readings on the absorption counter were noted. Water was then continuously aspirated through one capillary (through which aqueous standards were aspirated) and the diluted naphtha samples through the other and the corresponding per cent absorptions were noted.

The calibration curve (Fig. 1) was drawn between the concentrations of copper in aqueous standards and their corresponding per cent absorptions obtained at 10 times scale expansion. The apparent copper content in the diluted naphtha samples was noted from the above curve and was corrected for viscosity to get the actual copper content in naphtha samples.

Results and Discussion

The aqueous standard method for the estimation of iron in naphtha developed[2] during the study of miscible and immiscible organic liquids using a DCS was successfully adopted for the estimation of very low content of copper in some naphtha samples. As very low absorption was obtained, a scale expansion of ×10 was used. Copper was not detected in three samples whereas in the other six samples its concentration varies from 0.02 to 0.14 μg/ml. The use of MIBK for dilution of the samples was quite satisfactory as it gave a smooth burning of the flame. The present method is quite sensitive, rapid and economical and avoids the use of costly organometallic compounds which are not easily available. Petroleum products, other than naphtha, can also be analysed for impurities in them by this method.

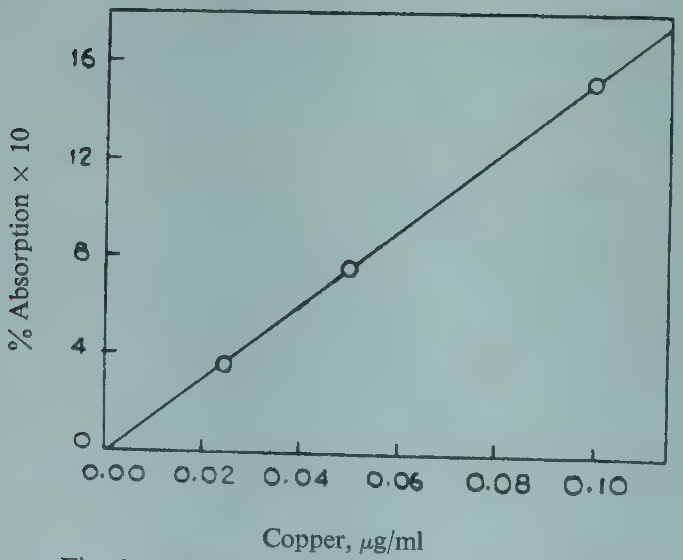

Fig. 1—Calibration Curve for Copper in Naphtha Obtained by Aspirating Aqueous Standards and MIBK Blank Simultaneously through the Lower Capillaries of DCS (1:1)

TABLE 1—CONCENTRATION OF COPPER IN NAPHTHA SAMPLES, μg/ml

Sample No.	Apparent Copper in the Diluted Sample C	Copper (Apparent) in Naphtha Sample C′ (C×5)	Copper in Naphtha after Viscosity Correction, (C′×0.59)
1.	0.046	0.230	0.14
2.	0.008	0.040	0.02
3.	—	—	—
4.	0.011	0.055	0.03
5.	0.025	0.125	0.07
6.	—	—	—
7.	—	—	—
8.	0.008	0.040	0.02
9.	0.020	1.000	0.06

— not detected

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[Original mss. received on Sept 20, 1973]

UDC 544.68: 549.222

A number of rock phosphate samples have been spectrographically analysed using d.c. arc for a number of trace and minor elements. Lead, copper, manganese, vanadium, titanium and sodium have been simultaneously determined by using cobalt as a single internal standard. The samples and the standards were diluted (1:1) with a buffer prepared by mixing specpure graphite powder and lithium carbonate in the ratio of 9:1. The presence of some other elements in these samples has also been indicated.

Simultaneous Estimation of Some Trace and Minor Elements in Rock Phosphates by Emission Spectrography

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Introduction

Rock phosphate is an important raw material for the production of phosphatic fertilizers and phosphoric acid. In powder form, it can also be applied directly to acidic soils. However, impurities present in it are carried into the fertilizer and finally added to the soil. The importance of a number of trace and minor elements in soils and fertilizer raw materials has already been discussed earlier[1,2].

The P_2O_5 contents of rock phosphates have been estimated by a number of workers[3-6] but little work has been done on the study of trace and minor elements present in them. Jacob *et al*[7] have given percentage of some elements in Florida phosphate. In the present work, the spectrographic method used for limestones[2] has been slightly modified and applied for the simultaneous estimation of some trace and minor impurities, viz. lead, copper, manganese, vanadium, titanium and sodium, in some rock phosphate samples. A new buffer (a mixture of graphite powder and lithium carbonate in the ratio of 9:1) has been selected instead of the graphite powder buffer used earlier. 0.9 per cent of cobalt mixed with the buffer has been satisfactorily used as a single internal standard for all the six elements estimated. Also, a number of other elements have been detected using a d. c. arc.

Experimental

Nine rock phosphate samples (2 imported and 7 Indian) from (1) Jordan, (2) Nauru, (3-5) Trombay (samples 1, 2 and 3), (6-8) Jodhpur (samples RS-121, RS-277 and apatite) and (9) Rajasthan were studied. They were finely powdered and dried in an oven.

Detection of Elements: A buffer was prepared for the present work by thoroughly mixing lithium carbonate (1 part) and graphite powder (9 parts), both of specpure quality. 100 mg. of the samples were mixed with equal amount of the above buffer and about 75 mg. of the mixtures were packed in the crater (5 mm. in diam. and 3 mm. deep) of the electrodes made from National ultra-purity graphite rods of 6.35 mm. diam. The upper electrode was kept 2.5 cm. long. The samples in the graphite electrodes were arced at 10 amp. (after being kept in oven at 100°C for 2 hr) and iron at 5 amp. The spectra were photographed on Illford N-30 plate, in the region of 2550-3500 Å on a Russian quartz spectrograph (KCA-1) using a slit width of 0.012 mm. and slit length of 1.7 mm. The exposure time was kept 45 sec. for the samples and 15 sec. for iron. The elements detected using the spectrum projector SP-2 are given in Table 1.

Estimation of Elements. For estimation work, a buffer internal standard (BIS) was prepared by mixing 0.9 per cent of specpure cobalt powder in the buffer prepared above. 100 mg of this BIS was mixed with equal amount of the samples and 75 mg of the mixture was packed in the electrode as above. For synthetic standards, a base was prepared by mixing Analar/specpure quality of calcium phosphate (94.0), silicon dioxide (3.0), ferric oxide

TABLE 1—ELEMENTS DETECTED IN ROCK PHOSPHATE SAMPLES

Sl. No.	Sample from	Elements detected
1.	Jordan	Ca, Si, Al, Fe, Sr, Mg, Ba, Na, Ti, Mn, V, Cu and Ni
2.	Nauru	Ca, Si, Al, Fe, Mg, Ba, Sr, Na, Ti, Mn, Cu, V and Cd
3.	Trombay (S-1)	Ca, Si, Al, Fe, Mg, Sr, Ba, Na, Ti, Mn, V, Cu and Ni
4.	Trombay (S-2)	Ca, Si, Fe, Al, Mg, Ba, Sr, Mn, Na, Ti, V and Ni
5.	Trombay (S-3)	Ca, Si, Al, Fe, Sr, Ba, Mg, Na, Ti, Mn, V and Cu
6.	Jodhpur (Rs-121)	Ca, Si, Fe, Al, Sr, Ba, Mg, Na, Mn, Ti, Pb, Cu and V
7.	Jodhpur (RS-277)	Ca, Si, Al, Fe, Mg, Ba, Sr, Na, Ti, Cu, Mn, V and Ni
8.	Jodhpur (Apatite)	Ca, Si, Al, Fe, Mg, Ba, Sr, Na, Ti, Mn, V, Cu, and Ni
9.	Rajasthan	Ca, Si, Al, Fe, Sr, Ba, Mg, Na, Ti, Mn, Pb, Cu and V.

NB: The amounts of elements are roughly in decreasing order (visual inspection).

TABLE 3—SELECTED ANALYTICAL LINE PAIRS

Sl. No.	Element	Wavelength, Å	Internal Standard Co-Wavelength, Å
1.	Pb	2833.069	2989.588
2.	Cu	3273.962	3283.462
3.	Mn	2949.205	2989.588
4.	V	3183.406	3154.794
5.	Ti	3199.915	3154.794
6.	Na	3302.323	3283.462

(1.5) and aluminium oxide (1.5) per cent respectively. Suitable quantities of specpure or Analar quality of salts (mostly oxides) of the elements to be estimated were mixed and 0.0405 g. of this was mixed with 0.3595 g. of the above base and 0.4 g. of BIS to get working standard No. 1. To prepare standard No. II. 0.25 g. of No. 1 was mixed with 0.25 g. of the base and 0.25 g. of BIS.

Similarly, four more standards were prepared by successive dilutions. A set of six standards (Table 2) was made to cover a wider range and for convenience for final selection of a set of 3 to 4 standards. 75 mg of these standards were packed in the crater of the graphite electrodes. All the electrodes packed with samples and standards were kept in an oven at 100°C for about 2 hrs, before being arced. All the spectra for iron, BIS, samples and standards were recorded on the same plate keeping the experimental conditions same as for the above detection work. After processing the plate, some analytical lines were marked by using the spectrum projector and the selected line pairs are given in Table 3. Using Hilger's non-recording microphotometer model L-450, the deflections for the lines of the elements (to be estimated) and corresponding cobalt line in standards were noted. The calibration curves were drawn between the logarithm of the ratio of the deflection for the analytical line pairs and the logarithm of the corresponding concentration of the elements in the standards. From the curves, the amounts of different trace and minor elements in the rock phosphate samples were noted (Table 4).

Results and Discussion

It is seen from Table 1 that nickel is present (in traces) in only five samples. Its lines were very faint in the spectra of these samples and so could not be measured on the microphotometer. Lead has been found (Table 4) only in Jodhpur (RS-121) and Rajasthan samples (32 and 15 ppm respectively). In one of the samples, viz. from Nauru, cadmium was detected but could not be estimated as its spectral lines were very faint.

From Table 4, it is also seen that copper content in the present samples varies from 12 to 71 ppm. Copper

TABLE 2—CONCENTRATION OF ELEMENTS IN SYNTHETIC STANDARDS, %

Sl. No.	Element	Std. I	Std. II	Std. III	Std. IV	Std. V	Std. VI
1.	Pb	0.1620	0.0540	0.0180	0.0060	0.0020	0.0007
2.	Cu	0.4050	0.1350	0.0450	0.0150	0.0050	0.0017
3.	Mn	0.4050	0.1350	0.0450	0.0150	0.0050	0.0017
4.	V	0.1012	0.0337	0.0112	0.0037	0.0012	0.0004
5.	Ti	0.2025	0.0675	0.0225	0.0075	0.0025	0.0008
6.	Na	0.4050	0.1350	0.0450	0.0150	0.0050	0.0017

TABLE 4—CONCENTRATION OF SOME ELEMENTS IN ROCK PHOSPHATE SAMPLES, %

Sl. No.	Sample from	Pb	Cu	Mn	V	Ti	Na
1.	Jordan	—	0.0026	0.0082	0.0051	0.0214	0.3236
2.	Nauru	—	0.0028	0.0056	0.0011	0.0174	0.1059
3.	Trombay (S-1)	—	0.0014	0.0102	0.0033	0.0380	0.2188
4.	Trombay (S-2)	—	0.0023	0.0653	0.0008	0.0174	0.0324
5.	Trombay (S-3)	—	0.0012	0.0200	0.0033	0.0355	0.0933
6.	Jodhpur (Rs-121)	0.0032	0.0015	0.0186	0.0012	0.0182	0.1950
7.	Jodhpur (RS-277)	—	0.0071	0.0050	0.0011	0.0776	0.1161
8.	Jodhpur (Apatite)	—	0.0013	0.0148	0.0016	0.0257	0.2455
9.	Rajasthan	0.0015	0.0013	0.0129	0.0013	0.0144	0.2818

being a micronutrient, its presence in these samples is advantageous; similarly, the presence of manganese, which varies from 50 to 653 ppm. While vanadium varies from 8 to 51 ppm, titanium varies from 144 to 776 ppm and sodium from 0.0342 to 0.3236 per cent.

In the present study, pure graphite buffer was found unsuitable as the arc burning was not smooth. Mixtures of graphite powder and lithium carbonate in different ratios were tried and finally a mixture with graphite powder and lithium carbonate in the ratio of 9:1 was selected as a buffer. It was found to be quite satisfactory for the present work.

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[Original mss. received on Dec. 26, 1973]

UDC 547.495+546.391.85: 541.118: 541.12.034

Pressure has an effect on the properties and reactivity of the binary system comprising urea and monoammonium phosphate (MAP). At elevated temperature monoammonium phosphate condenses to a complex mixture of ammonium polyphosphates and this in turn under pressure and temperature forms an adduct with urea.

Crystal Phase Characteristics of Residual Solids in the Reaction of Urea + MAP under Pressure and Temperature

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Introduction

The combined effect of pressure and temperature makes it possible to induce chemical reactions or phase transformations under appropriate conditions. The opposite, inhibition of normally occurring phase transition, is also possible by the action of pressure and temperature. As such, it appeared possible to induce some changes in the chemical and physical behaviour under pressure and temperature in the composition of urea and ammonium phosphate. Recently, there has been an increasing interest in an urea-ammonium phosphate complex. The product is a high analysis multinutrient fertilizer. Urea-ammonium phosphate complex fertilizer contains largely urea and monoammonium phosphate (MAP) or diammonium phosphate (DAP). In the earlier investigation[1] on this system it has been observed that urea does not form any additive compound with MAP or DAP in solid state under ordinary pressure and ambient temperature. However, in the solution state the existence of very unstable complex has been found and the instability constants were determined. The present work has, therefore, been exploratory in nature confined to the study of the reactivity of urea and MAP in solid state under pressure and temperature.

Experimental

The high pressure, high temperature apparatus used in this study was an autoclave (without stirrer), manufactured by Friedrich Uhde GmbH, and the specimen was inserted into electrically heated chamber to which pressure was transmitted by nitrogen gas medium. In the present experimental set-up investigation by x-rays of the materials involved during high pressure were not possible. Therefore, only the high pressure products which have sufficient stability could be analysed by x-ray diffraction after the release of the pressure.

Reagent grades of fertilizer salts, such as urea and monoammonium phosphate (MAP), were used directly from the stock bottles. Weighed mixtures of the component salts (urea and MAP in equal weights) were finely ground, dried and then introduced into the pressure chamber of the autoclave.

The specimens for x-ray diffraction analysis were used in the same condition as they came from the pressure chamber, with only light grinding. X-ray diffraction data and the chemical analysis are given in Tables 1 and 2 respectively.

Results and Discussion

In the present investigations, different sets of samples comprising the physical mixture of urea and monoammonium phosphates were studied under varying pressure and temperature. Equal weights of urea and MAP were mixed thoroughly and heated at 140°C in an air oven continuously for 12 hr. The sample, when analysed by x-rays, revealed that the product contained MAP as a major phase along with an unknown compound. It is to be noted, however, that from the x-ray

TABLE 1—X-RAY DIFFRACTION DATA OF UREA + MAP AT ELEVATED TEMPERATURE AND PRESSURE

At 140°C and Atmospheric Pressure for 12 Hours				At 140°C and 20 kg/cm² for 4 Hours				At 140°C and 50 kg/cm² for 4 Hours			
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
7.4	w	2.32	vw	9.75	f	2.22	vw	7.4	vvw	2.16	vw
6.2	vvw	2.25	w	7.5	f	2.15	vw	6.6	vvw	2.10	vw
5.75	vvw	2.22	w	6.8	f	1.85	vvw	6.4	vvw	2.05	vw
5.59	s	2.17	vvw	6.3	w	1.83	vvw	5.7	ms	1.98	vvw
5.32	s	2.14	vvw	6.00	m	1.74	vvw	5.5	s	1.86	vvw
4.62	vvw	2.12	vvw	5.6	mw	1.66	vw	5.00	m	1.84	vvw
4.42	vvw	2.06	vvw	5.4	ms			4.60	w	1.82	vvw
4.38	m	2.04	vvw	4.9	mw			4.35	vvw	1.75	vvw
4.28	m	2.001	m	4.8	f			4.00	mg	1.72	vvw
3.74	m	1.94	vvw	4.58	vvw			3.88	mw	1.67	vw
3.66	mw	1.90	f	4.30	vvw			3.85	vvw		
3.62	vvw	1.86	vvw	4.20	vvw			3.72	vw		
3.42	m	1.77	vw	3.98	s			8.62	w		
2.40	m	1.702	vw	3.85	vw			3.38	vw		
3.38	vvw	1.68	vvw	3.80	w			3.32	mw		
3.20	f	1.67	vvw	3.7	vvw			3.25	ms		
3.15	f	1.60	w	3.4	w			3.20	vvw		
3.07	vs	1.532	vw	3.38	vvw			3.15	mw		
2.93	vw	1.47	vw	3.30	m			3.12	vvw		
2.90	vvw	1.365	vw	3.20	m			3.05	m		
2.82	vvw	1.33	w	3.12	vw			2.96	vvw		
2.79	w	1.29	vvw	3.02	m			2.82	vvw		
2.66	vvw	1.25	vvw	2.82	vw			2.72	vvw		
2.65	m	1.22	vvw	2.80	vw			2.64	vvw		
2.62	vw	1.19	vvw	2.75	vvw			2.53	w		
2.56	vw			2.70	vvw			2.42	vw		
2.54	vw			2.62	vvw			2.40	vw		
2.50	w			2.50	mw			2.32	vvw		
2.46	vvw			2.40	vw			2.28	vw		
2.43	vw			2.38	vvw			2.23	vvw		
2.36	w			2.28	w			2.20	vvw		

TABLE 2—EFFECT OF TEMPERATURE AND PRESSURE ON THE COMPOSITION OF UREA AND MONOAMMONIUM PHOSPHATE (1:1 BY WEIGHT RATIO)

(Calculated N = 28.84, %)
(,, P = 13.21, ,,)

Condition		X-ray Analysis	Chemical Analysis	
Temperature	Pressure		% N	% P
Room Temp.	Open atmosphere	Urea & MAP both are present. No change	28.817	13.19
140°C	,,	Urea absent. MAP present along with a complex mixture of Ammonium Polyphosphate	24.06	13.71
Room Temp.	50 kg/cm²	Urea & MAP both are present. No change	28.782	13.126
140°C	20 kg/cm²	Urea & MAP both are absent. An unknown phase is formed.	25.21	13.472
140°C	50 kg/cm²	Urea present, MAP absent. An unknown phase is also present.	26.736	—

powder pattern, no evidence of urea was found. Urea decomposes around this temperature. Also, it is known that MAP begins to lose ammonia at 160°C and above 185°C loses ammonia and water and then condenses to a complex mixture of ammonium polyphosphate. Shen and Shahlheber[2] have prepared ammonium polyphosphate by mixing urea and MAP in equimole ratios and heating at 135°C for 12 hr and they claim that the product was substantially water-insoluble ammonium polyphosphate. Therefore, in the present investigation, the presence of a new phase can be attributed to the formation of a complex mixture of ammonium polyphosphates. This is also evident by the x-ray pattern of the sample. The excess amount of MAP in the mixture remained unreacted.

Again, the mixture of urea and MAP, 1:1 by weight ratio, was subjected to a pressure of 50 kg/cm² at 140°C for 4 hr and the sample was analysed by x-rays. The product contained a substantial amount of urea along with the formation of a new compound, the x-ray pattern of which was dissimilar with the earlier sample heated at atmospheric pressure. MAP was totally absent. It is well-known that urea melts at 133°C and decomposes at higher temperature to ammonia and carbondioxide. At elevated temperature (130-150°C) and high pressure (35 atm.) ammonia and carbondioxide react to produce urea.

$$CO(NH_2)_2 \xrightarrow[\text{133°C}]{\text{at atm.}} NH_3 + CO_2 \xrightarrow[\text{and 130-150°C}]{\text{at 35 atm.}} CO\ (NH_2)_2$$

Therefore, when the mixture of urea and MAP was subjected to a pressure of 50 kg/cm² at 140°C which are the ambient pressure and temperature of urea synthesis, the decomposition of urea was inhibited. Hence, the product contained larger amount of urea. It is possible that MAP might have been polymerized to form a complex mixture of ammonium polyphosphates at this pressure and temperature. The experiment was repeated at a reduced pressure, viz. 20 kg/cm², and 140°C for 4 hr. Surprisingly, the product did not contain both urea and MAP. X-ray pattern of the product was entirely different from that of the components as well as the new phase existing along with urea in the previous sample. Chemical analysis of these samples did not show any appreciable changes in their composition except some percentage of nitrogen loss. It seems probable, therefore, that urea is forming an adduct with ammonium polyphosphate due to the fact that pressure had affected the reactivity of the solid state system of urea and MAP. Further work is in progress for elucidating the crystallo-chemical properties of this compound.

Acknowledgements

The authors are thankful to Sri Mohan for his assistance in the experimental set-up of high pressure apparatus. Their thanks are also due to Dr. S. S. Chatterjee and Sri S. C. Chatterjee for the chemical analysis of the samples.

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[Original mss. received on Oct 30, 1972]

UDC 543.72: 546.185—31

A number of weak acids and alkalies have been shown to be capable of dissolving secondary and tertiary phosphates of magnesium, calcium, strontium, barium, zinc, manganese, nickel and cobalt to a greater extent than water. The P_2O_5-solubility of all these phosphates increases invariably with the increase in the concentration of the acids and alkalies, and the solubilization action varies in the order: citric acid > tartaric acid > acetic acid > carbonic acid in the case of acids and sodium hydroxide > sodium carbonate > sodium bicarbonate in the case of alkalies. The increase in solubility of these sparingly-soluble phosphates in weak acids in due to the solvent action and complex-forming nature of the anions of the acids and as the structure of the acids affects both the solvent action and the ability of the anion to form complex compounds, solubilization is influenced to a large extent by the same. In the case of alkalies it is due to the decomposition of the phosphates.

Solubilization of Sparingly Soluble Phosphates in Weak Acids and Alkalies

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As the availability of phosphates to plants depends upon the extent of their solubility in soil solutions, the solubility of various sparingly soluble phosphates in weak acids and alkalies aroused the interest of a large number of chemists[1–5]. A systematic study on the solubility of the phosphates of magnesium, calcium, strontium, barium, zinc, manganese, nickel and cobalt in carbonic, acetic, tartaric and citric acids and in sodium bicarbonate, sodium carbonate and sodium hydroxide solutions has, therefore, been carried out to assess their utility under different soil conditions.

Experimental

Calculated amounts of secondary and tertiary phosphates of magnesium, calcium, strontium, barium, zinc, manganese, nickel and cobalt, containing 0.5 per cent P_2O_5, were taken in a number of 250 ml pyrex glass stoppered conical flasks. 100 ml of carbonic, acetic, tartaric and citric acid solutions and sodium bicarbonate, sodium carbonate and sodium hydroxide solutions of varying normality were added to these flasks and the contents shaken in a mechanical shaker for 1 hr and then allowed to stand for 24 hr at 30°C in a thermostat. After 24 hr the solutions were filtered and analysed for the P_2O_5 content[6]. The phosphates used were prepared by the precipitation method[7].

Discussion

The results (Table 1) indicate that the solubility of all these phosphates even in very dilute solutions of acids and alkalies is more than their solubilities in water alone[8]. The solubilization action of the acids varies in the order of citric acid > tartaric acid > acetic acid > carbonic acid and of alkalies sodium hydroxide > sodium carbonate > sodium bicarbonate.

The increase in solubility of all these phosphates in weak acids can be attributed to two factors, viz. (i) acid solvent action and (ii) the complex-forming capacity of the anions of the acids. The dissociation constants of the acids[9] reveal that carbonic acid is a much weaker acid followed by acetic acid, and this appears to be the reason that the solubility of phosphates is least in carbonic acid followed by that in acetic acid. But the dissociation constants do not seem to explain the higher solubility of phosphate in citric acid in comparison to tartaric acid. It seems that complex formation between the phosphates and the acid takes place and the amount of soluble P_2O_5 depends on the stability of the complex formed between the phosphates and the anion of the acid. The more the stability of the complex more will be the amount of P_2O_5 released into the solution. It, therefore, appears that citrate anion has the capacity to form more stable complexes with metallic cations of the phosphates than

TABLE 1—SOLUBILITY OF PHOSPHATES IN WEAK ACID & ALKALIES AT 30°C, P_2O_5 g/l

Secondary Phosphates								Solvents	Tertiary Phosphates							
Mg	Ca	Sr	Ba	Zn	Mn	Ni	Co		Mg	Ca	Sr	Ba	Zn	Mn	Ni	Co
								Carbonic Acid								
0.5609	0.1519	0.1505	0.0460	0.0809	0.0213	0.0156	0.0170	0.0012N	0.3748	0.2726	0.1533	0.0766	0.0823	0.0142	0.0198	0.0284
0.7739	0.2371	0.2414	0.0951	0.1150	0.0326	0.0255	0.0284	0.0030N	0.6162	0.4899	0.2470	0.1150	0.1178	0.0191	0.0298	0.0411
0.9386	0.2953	0.2840	0.1192	0.1377	0.0397	0.0298	0.0346	0.0060N	0.7980	0.6588	0.3053	0.1448	0.1505	0.0241	0.0355	0.0454
								Acetic Acid								
0.6177	0.1846	0.1576	0.0482	0.0852	0.0227	0.0170	0.0184	0.0012N	0.4402	0.3237	0.1803	0.0823	0.0880	0.0156	0.0213	0.0298
0.7895	0.2414	0.2201	0.0979	0.1207	0.0355	0.0284	0.0312	0.0030N	0.6361	0.4970	0.2371	0.1207	0.1306	0.0213	0.0326	0.0482
0.9428	0.3337	0.2982	0.1391	0.1576	0.0440	0.0326	0.0369	0.0060N	0.8406	0.7014	0.3251	0.1562	0.1647	0.0284	0.0397	0.0553
								Tartaric Acid								
0.9741	0.3280	0.2186	0.0511	0.1476	0.0269	0.0248	0.0262	0.0012N	0.8775	0.6517	0.3180	0.0894	0.1547	0.0241	0.0255	0.0431
1.0848	0.4373	0.2740	0.0908	0.1775	0.0397	0.0347	0.0355	0.0030N	0.9911	0.7526	0.3379	0.1263	0.1803	0.0340	0.0383	0.0511
1.2240	0.5893	0.3408	0.1491	0.2073	0.0539	0.0440	0.0454	0.0060N	1.1374	0.8917	0.3621	0.1704	0.2115	0.0426	0.0525	0.0568
								Citric Acid								
1.0820	0.5494	0.2726	0.0766	0.1945	0.0582	0.0497	0.0511	0.0012N	0.9869	0.8576	0.3450	0.0908	0.2030	0.0468	0.0553	0.0582
1.2410	0.6546	0.3294	0.1292	0.2101	0.0667	0.0610	0.0653	0.0030N	1.1644	0.9712	0.3777	0.1240	0.2314	0.0582	0.0660	0.0695
1.4725	0.7952	0.3976	0.1931	0.2428	0.0781	0.0724	0.0738	0.0060N	1.3972	1.1161	0.4174	0.1959	0.2627	0.0695	0.0766	0.0823
								NaOH								
0.4813	0.1501	0.1495	0.0458	0.0733	0.0210	0.0150	0.0165	0.0012N	0.3627	0.2214	0.1503	0.0710	0.0808	0.0140	0.0190	0.0275
0.4853	0.1541	0.1535	0.0498	0.0773	0.0250	0.0190	0.0205	0.0030N	0.3667	0.2252	0.1543	0.0750	0.0848	0.0180	0.0230	0.0315
0.4917	0.1605	0.1599	0.0562	0.0837	0.0314	0.0254	0.0269	0.0060N	0.3731	0.2316	0.1607	0.0814	0.0912	0.0240	0.0294	0.0379
								Na_2CO_3								
0.3321	0.1037	0.1120	0.0439	0.0643	0.0191	0.0134	0.0146	0.0012N	0.2847	0.1525	0.1314	0.0572	0.0685	0.0125	0.0175	0.0206
0.3351	0.1067	0.1150	0.0469	0.0673	0.0221	0.0164	0.0176	0.0030N	0.2877	0.1555	0.1344	0.0602	0.0715	0.0155	0.0205	0.0236
0.3399	0.1115	0.1198	0.0517	0.0721	0.0269	0.0212	0.0224	0.0060N	0.2925	0.1603	0.1412	0.0650	0.0763	0.0203	0.0253	0.0284
								$NaHCO_3$								
0.3053	0.0794	0.1093	0.0433	0.0613	0.0171	0.0123	0.0138	0.0012N	0.2814	0.1492	0.1232	0.0561	0.0663	0.0115	0.0165	0.0194
0.3080	0.0821	0.1120	0.0460	0.0640	0.0198	0.0150	0.0165	0.0030N	0.2841	0.1519	0.1259	0.0588	0.0680	0.0142	0.0192	0.0221
0.3125	0.0866	0.1165	0.0505	0.0685	0.0243	0.0195	0.0210	0.0060N	0.2886	0.1564	0.1304	0.0633	0.0725	0.0197	0.0237	0.0266

tartrate anion. This explains the higher solubility of phosphates in citric acid as compared to tartaric acid.

The solubility of various phosphates in alkaline solutions is controlled by the solubility products of their respective hydroxide. Sodium carbonate and sodium bicarbonate both yield $(OH)^-$ ions when dissolved in water, but the concentration of $(OH)^-$ ions is less than in the case of sodium hydroxide. When these $(OH)^-$ ions come in contact with the metallic ions from the phosphates, the respective hydroxides are precipitated, when their ionic concentrations exceed their solubility products. More $(OH)^-$ ions lead to the formation of more metallic hydroxides from the phosphates resulting in more liberation of phosphoric acid into the solution. This explains the strong decomposing action of sodium hydroxide followed by these of sodium carbonate and sodium bicarbonate.

The results conclusively show that organic acids, like acetic, tartaric and citric, which are formed during the slow oxidation of organic matter as intermediate products are more responsible than the final product carbonic acid in making phosphate available to crops in soils. On the other hand, fertilizers, like basic slag and rock phosphates, containing secondary and tertiary phosphates of calcium, magnesium, etc. may be utilized in the reclamation of alkali soil, as mono-phosphate produced during the hydrolysis of these fertilizers[2] can readily convert sodium carbonate and sodium bicarbonate present in the alkali soil into sodium hydrogen phosphate and metallic carbonate and bicarbonate resulting in the improvement of the soil by removing the harmful effects of alkali carbonates.

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[Original mss. received on Sept. 20, 1973]

EDITOR'S NOTE

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UDC 544.6: 546.73: 546.881

Hydrated cobalt metavanadate consisting of VO_5 trigonal bipyramidal chains undergoes a structural transformation on heating. The anhydrous cobalt metavanadate, thus obtained, consists of VO_4 tetrahedral chains. This structural transformation has been identified by IR spectroscopic studies.

IR Studies of Hydrated and Anhydrous Cobalt Metavanadate

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Introduction

Trigonal bipyramid, tetrahedron or square pyramid are the three types of coordination known to be characteristic of quinquevalent vanadium with oxygen. The particular configuration adopted by any V-O compound depends upon the type of hybridization involved.

Metavanadates of alkali metals are known to exist in two of the three possible structures for V-O compounds, i.e. with trigonal bipyramidal or tetrahedral coordinations[1]. All anhydrous metavanadates, except sodium metavanadate are isostructural with ammonium metavanadate with tetrahedral chains, while the structures of the hydrated metavanadates exhibit trigonal bipyramidal chains. Because of this structural dissimilarity between the hydrated and anhydrous forms, most of the hydrated metavanadates undergo structural transformations during the loss of water.

Bhattacharyya *et al*[2] have observed in their x-ray studies that cobalt metavanadate hydrate undergoes a structural transformation around 270°C on complete dehydration of the sample. The present investigation concerns the study of the transformation in cobalt metavanadate using I.R. absorption spectral analysis.

Experimental and Results

The hydrated cobalt metavanadate was prepared by the same procedure as followed by Bhattacharyya *et al*[2]. However, on analysis, the compound was found to have the composition $Co(VO_3)_2.2H_2O$ and not 2 $Co(VO_3)_2.5 H_2O$, as reported by Bhattacharyya *et al.* The anhydrous cobalt metavanadate was obtained by heating the hydrated sample at 400°C to a constant weight. The IR absorption spectra of the two samples were recorded in a Beckman IR-12 using the KBr pellet technique.

Because of the structural differences, the two forms of the cobalt metavanadate can be expected to give rise to two dissimilar IR absorption spectra. The observed IR absorption bands are summarized in Table 1.

TABLE 1—IR Spectral Maxima for $Co(VO_3)_2.2H_2O$ and $Co(VO_3)_2$

Sample	Absorption Maxima, cm^{-1}	Intensity	Assignment
$CO(VO_3)_2.2H_2O$	980, 940	Medium	V-O terminal
	850	Medium	V-O bridged
	650	Medium	Co-O
$Co(VO_3)_2$	860	Strong	V-O terminal
	680	Strong	Co-O
	550	Medium	V-O bridged

An assignment of the bands observed can be attempted on the basis that the hydrated metavanadate has a trigonal bipyramidal chain structure while the dehydrated form contains tetrahedral chains. In the former structure, each vanadium atom is connected to five oxygen atoms to form a distorted trigonal bipyramid and these bipyramidal polyhedra share edges to form continuous chains. Hence, in each bipyramidal unit of such a structure, there are two types of V-O bonds. Three oxygen atoms, each of which connect two vanadium atoms and are shared by two polyhedra, form the first type. The remaining two oxygen atoms are bonded directly to the vanadium atoms, thus giving rise to a second type of V-O bond. Such a structure can result only from d^3sp hybridization.

The bonds observed at 980, 940 and 850 cm^{-1}, for the hydrated sample, can be assigned to these two different types of V-O bonds. Of the two, the V-O-V bonding is longer and hence should give to an absorption maximum at a lower frequency. The band at 850 cm^{-1} can thus be attributed to the V-bridged oxygen bonds. The bands at 980 and 940 cm^{-1} are due to the shorter V-terminal oxygen bonds.

On the other hand, a d_ϵ^3s hybridization around vanadium, would give rise to a tetrahedral structure. In this structure, chains of tetrahedra are connected through their apices and are similar to the pyroxene silicate chains. The coordination through the d_ϵ^3s hybridized orbitals also give rise to two types of V-O bonds. One consists of V-terminal oxygen bonds and other involves V-bridged oxygen bonds. The two bands observed at 860 and 550 cm^{-1} in the case of the dehydrated cobalt metavanadate can be assigned to the shorter V-terminal oxygen bonds and the longer V-bridged oxygen bonds respectively. Both systems give rise to a band at 650 cm^{-1} which can be assigned to the Co-O bond.

The IR spectral study of the anhydrous and the hydrated cobalt metavanadate clearly indicates that the transformation involves a change in the coordination type of V(V) from trigonal bipyramidal to tetrahedral. The assignments of IR absorption bands are in general accord with those reported by Olivier for chromium metavanadate[3] and Dupuis and Lorenzelli[4] for metavanadates of K, Ag, Ca, Sr and B[5].

Acknowledgements

Grateful thanks are due to Professors M.V.C. Sastri and V. Srinivasan for their kind interest and encouragement and to Dr. G. Aravamudan for helpful discussions. This work forms part of a research project sponsored by the National Bureau of Standards, Washington D. C. under Contract No. NBS(G)-133. One of the authors (P.N.) is thankful to the C.S.I.R. (India) for the award of a Research Fellowship.

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[Original mss. received on Nov. 6, 1973]

UDC 633.18 : 632.9

The effect of top dressing with different ameliorative and manurial treatments on the control of bronzing disease in rice after the manifestation of symptoms was investigated during the second crop season of 1971-72. The results indicated that the disease could be effectively checked by top dressing with lime.

Studies on the Control of Bronzing Disease in Rice *(Oryza Sativa L.)*

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Bronzing disease is causing heavy damage to the rice crop in the waterlogged acid soils of Kerala and assumes menacing proportions when high-yielding dwarf *indica* varieties are cultivated. The disease is considered to be related to physiological disorders associated with excess of iron and other harmful substances in ill-drained acid soils. Ota and Yamada[1], Ponnamperuma[2] and Sahu[3] have suggested that the disease incidence could be prevented by the application of sufficient quantity of lime before flooding to keep the soil pH close to neutrality. According to Ponnamperuma[2], 7.5-15 tons of slaked lime would be required per ha in a lateritic soil having a pH 4-4.3. Application of so heavy a dose of lime is neither feasible nor economical. Therefore, investigations were carried out in the 2nd crop season (September-January) of 1971-72 at the Rice Research Station, Pattambi to evaluate the effectiveness of top dressing with different ameliorative and manurial treatments (including smaller doses of lime) on the control of bronzing disease in rice after the manifestation of symptoms.

Experimental

A standing crop of *Aswathy* rice of 120 days duration in an ill drained wet land field which contracted an uniform incidence of the disease was selected for the studies. The crop planted on 26.9.1971 with 26 days old seedlings received 5000 kg green leaf and 40 kg each of nitrogen, phosphate (P_2O_5) and potash per ha as basal dressing. Bronzing symptoms more or less similar to those described by Ponnamperuma[2] were noticed 18 days after transplanting. Obvious of these were discolouration of the older leaves starting at the tip and spreading along the leaf margin and brown spots on the upper half of the laminae of the older leaves. The tint of the affected leaf was orange. As the disease progressed, the affected leaves dried up giving the plant a scorched appearance. Growth and tillering of the affected plants were poor and the root system was scanty, coarse and dark brown. On chemical analysis the affected plants showed lower percentage values of nitrogen, phosphorus and potassium than healthy plants (N 1.100-1.210, P 0.723-0.952 and K 1.450-1.800).

The soil of the experimental plot was a lateritic loam having 0.89 per cent organic carbon, 21.4 kg and 104.8 kg respectively per ha of available phosphorus and potash and a pH of 5.9 at the time of disease incidence.

The experiment was laid out in randomized block design with 18 treatments (Table 1) and 3 replications. The treatments were applied on 22.10.1971 (26 days after transplanting).

The effect of different treatments on ferrous iron concentration in the soil solution 7 days after their application and on grain yield at maturity were determined.

Results and Discussion

The results (Table 1) revealed that the grain yields due to soil application of 1000 kg. CaO/ha (Treatment 2) and foliar spray of 40 kg. N/ha through urea (Tr. 4) were statistically on par and significantly outyielded all other

TABLE 1—Effect of Different Treatments on Grain Yield and Ferrous Iron Concentration in the Soil

Treatment, per ha	Grain Yield, kg/ha	Increase or Decrease over Control, %	Mean Fe^{2+} 7 Days After Treatment, ppm
1. Control	4032	—	200
2. 40 kg N as ammonium sulphate (soil)	4368	+ 8.3	230
3. 40 kg N as urea (soil)	4661	+15.6	220
4. 40 kg N as urea (foliar spray in two equal doses at one week interval)	4872	+20.8	135
5. 40 kg P_2O_5 as super phosphate (soil)	4116	+ 2.1	195
6. 80 kg P_2O_5 as super phosphate (soil)	4641	+15.1	225
7. 40 kg K_2O as muriate of potash (soil)	4242	+ 5.2	125
8. 80 kg K_2O as muriate of potash (soil)	4620	+14.6	80
9. 40 kg each of P_2O_5 and K_2O (soil)	4452	+10.4	135
10. 500 kg Cao as quick lime (soil)	4452	+10.4	130
11. 1000 kg CaO as quick lime (soil)	4914	+21.9	60
12. 1500 kg CaO as quick lime (soil)	4620	+14.6	85
13. 2000 kg CaO as quick lime (soil)	4494	+11.5	80
14. 40 kg K_2O as woodash (soil)	4662	+15.6	160
15. 40 kg N as farm yard manure (soil)	4074	+ 1.0	215
16. 4000 kg red upland soil (soil)	3990	− 1.0	240
17. 20 kg Mn as Mn SO_4 (soil)	3560	−11.7	145
18. Draining the field	4048	+ 0.4	155
C.D. (0.05)	128.8	—	—

treatments (21.9 and 20.8 per cent respectively over control). The effect of calcium was positive and significant upto 1000 kg CaO/ha and beyond that level it declined. This decline in yield may be due to direct injury to the plants or adverse effects of nutrient interactions. Liming reduced the toxic concentration of iron in the soil solution, possibly due to a rise in soil pH. Response due to nitrogen applied through fertilizers was significant. The effects due to two sources of fertilizer nitrogen (Trs 2 and 3) as well as two methods of urea application (Trs 3 and 4) were significant. Thus, the superiority of urea over ammonium sulphate and foliar application of urea over soil application under unfavourable soil conditions, are evident in the results. Ota and Yamada[1] and Sahu[3] have reported similar results. Influence of phosphorus on grain yield was significant only at the higher level. (80 kg. P_2O_5/ha).

The grain yield response due to potash was significant at both the levels (40 and 80 kg. K_2O/ha) tried. Potash also appeared to have reduced the ferrous iron concentration in the soil solution. Besides enhancing its utilization by plants, application of potash might have helped to liberate fixed ammonia in the soil, thereby increasing the soil pH[4] and suppressed the active iron concentration in the soil solution. The effect of 40 kg. K_2O/ha applied through wood ash (Tr. 14) was on a par with 80 kg. K_2O/ha applied through muriate of potash, which is attributable to the presence of phosphorus and calcium in addition to potassium in wood ash. Effective drainage was not possible due to the low-lying nature of the field.

The affected crop favourably responded to calcium, nitrogen, phosphorus and potassium. A possible rise in soil pH due to liming and a consequent reduction in the toxic concentration of iron and other harmful substances in the soil solution might have helped root development, absorptive function of roots and availability of nutrients to plants, resulting in higher yield. The inhibition of absorptive function of roots due to the disease has caused the deficiency of nitrogen, phosphorus and potassium in plants and topdressing of these nutrients has given response. The results clearly suggest that liming the soil even after the manifestation of symptoms is effective in the control of bronzing disease in rice.

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[Original mss. received on Aug. 10, 1973]

UDC 597.5: 591.23: 582.28

Eleven fungal species have been isolated from four species of fresh water fishes, commonly found in Gorakhpur (U.P.). These fungi are generally present in the soil and air adjoining the ponds.

Fungi from the Alimentary Canals of Some Fresh Water Teleosts

By R. S. KANAUJIA* AND S. SRIVASTAVA†

Introduction

With the studies of Bhargava *et al*[1], Clinton[2], Coker[3], Davis and Lazar[4], Nigrelli[5], Scoh and Bier[6] and Smith[7], the pathogenesis in fishes by fungi is well established. Previous reports, however, are confined to the few aquatic fungi which have usually been isolated as ecto-wound-parasites. No report is available on the presence of fungi in the alimentary canal of fishes and this has been presented in this communication.

Materials and Methods

Four species of teleosts of different groups and feeding habits (listed below), commonly found in Gorakhpur (U.P.) area have been selected for the present study.

Fishes: 1. Mystus vittatus, 2. Heteropneustes fossilis, 3. Channa striatus, 4. Anabas testudienus.

Order: 1. Cypriniformes, 2. Cypriniformes, 3. Ophiocephaliformes, 4. Perciformes.

Feeding Habit: 1. Omnivorous, 2. Omnivorous, 3. Carnivorous, 4. Omnivorous.

Abbreviation: 1. MV, 2. HF, 3. CS, 4. AT.

The fishes were caught alive and brought to the laboratory. For assessment of the fungi from their alimentary canals, they were thoroughly washed in several changes of sterilized distilled water. Their digestive tracts were dissected out separately with the help of sterilized scissors and forceps. The whole digestive tract was washed again with sterilized distilled water and then cut into small pieces. These pieces were aseptically transferred in sterilized conical flasks containing sterilized distilled water. The flasks were hand shaken for 15 min. and the suspension, thus obtained, was separately inoculated in *petri* dishes containing acidified Czapek's medium (pH 5). The dishes were incubated at room temperature for 8 days and the fungal colonies appearing on them were examined for studying the quality of the spores, they produced. The isolates were then purified and maintained on agar slants for further studies.

The survival of fungal isolates, viz. *Rhizopus nigricans*, *Aspergillus flavus*, *A. sydowi*, *Cladosporium epiphyllum*, *Penicillium* species, *Curvularia tetramera* and *Fusarium nivale* in alimentary canal was also studied. Before acclimatization the fishes were washed with sterilized distilled water. Acclimatisation was done in 1.5 × 1.0 × 1.5 feet sized aquaria. The water of the aquarium was replaced by fresh sterilized distilled water every 24 hours. The fishes were starved till no excreta was found in the aquaria. After 10 days small pieces of sterilized earthworms packed with spores of fresh cultures of test fungi inside their alimentary passage were provided to these fishes. The excreta recovered from each aquarium after 48 hours was collected gently and tested for the presence of fungal spores as usual and also under microscope by direct observation. After 96 hours, the fishes were taken out and washed gently with sterilized distilled water.

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Their alimentary canals were tested for presence of fungal spores by the methods described earlier. In the control set of experiment no fungus was supplied to the fishes.

Results

In all eleven fungal species were isolated from all the four species of fishes. Phycomycetes were only represented by 1 species. 10 species belonged to Deuteromycetes and 1 to *mycelia sterilia.* 2, 4, 7 and 8 species were recovered from CS, AT, MV and HF respectively; *Aspergilli* were in majority. The detailed data are presented in Table 1.

TABLE 1—Fungal Species Isolated from the Digestive Tracts of Certain Teleosts

Fungal Species	Fresh Water Teleosts				Control
	C. Striatus	*A. Testudineus*	*M. Vittatus*	*H. Fossilis*	
Rhizopus nigricans	−	−	−	+	−
Trichoderma viride	−	+	−	−	−
Aspergillus flavus	+	+	+	+	−
A. sydowi	−	+	−	+	−
A. niger	+	−	+	+	−
A. aculeatus	−	−	+	+	−
Penicillium sp.	−	−	+	−	−
Cladosporium epiphyllum	−	+	+	+	−
Curvularia tetramera	−	−	+	+	−
Fusarium sp.	−	−	+	−	−
White sterile fungus	−	−	−	+	−
No. of fungi	2	4	7	8	

+ present
− absent

Only *R. nigricans* could not survive, when fed to the starved fishes. *A. flavus, C. epiphyllum* and *F. nivalve* were found in all the fishes after passing through their digestive tracts, whereas rest of the fungi behaved differently in different fish species. No fungus could be detected from control (Table 2).

TABLE 2—Survival of Fungal Species in the Alimentary Canals of Certain Teleosts

Fungal Species	Fresh Water Teleosts				Control
	C. Striatus	*A. Testudineus*	*M. Vittatus*	*H. Fossilis*	
Rhizopus nigricans	−	−	−	−	−
Asperigillus flavus	+	+	+	+	−
A. sydowi	−	−	+	+	−
Cladosporium epiphyllum	+	+	+	+	−
Penicillum sp.	−	+	+	+	−
Curvularia tetramera	−	−	−	+	−
Fusarium nivale	+	+	+	+	−
No. of fungi	3	4	5	6	

+ present
− absent

Discussion

The number of the fungal species isolated from different fishes, differed. A higher number of isolates was noticed in HF and MV and the lowest from CS. This has again been confirmed with the studies conducted in laboratory conditions (Table 2). The possible cause for this diversity may be assigned to the different feeding habits of the teleosts. Comparatively low fungi were exhibited by AT, an omnivorous fish for which no interpretation can be put forth with the results of the present study. The fungi isolated in the present study are generally present in soil[8-12] and air[13-15]. The fungi present in the air and the soil adjoining the ponds and lakes get suspended in water. They are ingested by the fishes while preying and consequently reach the alimentary canal and pass through rectum with excreta. Fungi with generally thicker walls remain unaffected and have been found viable in the present study.

Acknowledgements

The authors are thankful to Prof. K. S. Bhargava and Prof. H. S. Choudhary, Heads, Departments of Botany and Zoology, University of Gorakhpur, Gorakhpur, respectively for providing the necessary laboratory facilities and to Dr. R. R. Mishra for criticism.

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[Original mss. received on July 14, 1973]

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UDC 66.02: 546.226.35 (540)

Sulphuric acid production is an age-old industry. Its technology is fast changing and developing. Though the fundamental concept remains the same when Philips first proposed in 1831 the oxidation of sulphur dioxide to trioxide over a catalyst bed, the techniques for effecting this conversion and absorbing the resultant sulphur trioxide gas have undergone radical changes. This technology can adopt various raw materials like sulphur, pyrites, gypsum and metallurgical gases. Sulphuric acid is also obtained as a by-product in the extraction of valuable metals, like zinc, copper, lead, cadmium and cobalt, etc. The routes for preparing a suitable SO_2/O_2 gas mixture for oxidation are many and diverse in nature and form a separate topic by itself. This paper is restricted in scope to a study of sulphuric acid plants based on sulphur.

Design Aspects of Sulphuric Acid Plants and the Associated Problems in Indian Industry

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Typical Operating Problems

A sulphur-based sulphuric acid plant is generally considered trouble-free. However, there are many problems in its operation, which stem from some false economy envisaged by some designers at the design stage of the plants. Faulty selection of materials and equipment and the omission of certain significant facilities like a proper storage for sulphur are the typical reasons for low production and frequent shut-downs. In one plant due to bad uneven flooring in the storage, the payloader scooping the sulphur was also feeding heavy quantities of concrete and earth to the sulphur melters. Thus solid impurity content was well above the design tolerances of the sulphur filter, with the result that fine solids were passing with the gas stream and were finally getting deposited on the first bed of the 4-bed catalytic converter, the exit gas from which was used to raise the temperature of the gas at the I bed inlet to the desired temperature level for the conversion of sulphur dioxide. Due to the blockage of the catalyst by the carry-over solids, the conversion was affected which also had serious repercussions on the performance of the heat exchanger. To maintain the terminal temperature of the heat exchangers, the inlet temperature of I bed had consequently to be increased by giving more hot gas from the boiler by-pass line. Naturally the overall conversion was reduced, leading to the problem of excessive sulphur dioxide in the stack and a bad environment.

The foregoing example is typical of how the trouble from one small area of the plant was transferred to each and every equipment and led to improper operation, loss of production and pollution. Such problems can be effectively overcome if a little foresight is used and certain liberal provisions are made in the plant at the design stage itself. Only if a covered sulphur storage and a gas filter had been provided in the design, the operation of the entire plant would have been streamlined. Due to heavy rains in that particular area a covered storage is desirable.

The problems of any operating unit can be generalized into two main groups due to: (1) faulty selection of material and equipment and (2) wrong design parameters for the plant.

In the Indian context, the first group of problems are further aggravated due to the non-availability of standard products. A typical example of this is the non-availability of quality cast iron pipes for the acid coolers. These coolers are invariably the major headaches of the maintenance engineer in any acid plant. Cast iron pipes for this service should have a uniform thickness, free from blow holes and chaplets, must have a fine grain structure and should strictly adhere to the desired chemical composition. But it is observed that there are only one or two parties in India who can supply pipes as outlined above, and in their case also the delivery schedule is quite prolonged, perhaps due to the essentially small scale facilities of theirs. Though in small plants these coolers will continue to be used, for large capacity plants it may be desirable to go in for alternate designs in stainless steel with cathodic protection, to ensure smooth operation of the plant.

A similar problem is faced in the high temperature load-bearing parts of the converter. The catalyst layers are supported on grids placed upon beams. In bigger converters the beams are supported centrally on a column. Thus, the central column and the grids have to withstand the effects of high temperature, load and corrosion. As creep becomes a significant force to be reckoned with under these extreme conditions, cast iron or proprietary alloys, like Meehanite, are preferred over various grades of steel and alloy steel. Chrome cast iron conforming to IS-3355 Gr. E is the preferred material. However, the control of Chromium content in the castings is quite irregular and the general quality of workmanship is not quite encouraging.

Design Considerations: The design parameters of the plant should also be carefully studied while the design is undertaken. The absolute humidity of atmospheric air is much higher in India than in Europe or USA. The general trend abroad is to make the drying and absorption towers identical. However, under Indian conditions the volume of packing required for air drying is larger than that for SO_3 absorption. Hence, if both towers are made identical, they should both be sized according to the air drying tower. Failure in this respect results in excessive moisture in the process gas, which leads to excessive mist formation and consequent maloperation. Many plants in India suffer from the trouble with excessive moisture in the gas stream, and in certain cases modifications were necessary to somewhat reduce the problems.

Another significant factor is the quality of sulphur. When a plant using yellow sulphur switches on to the black variety the above problems are encountered. Black sulphur has an appreciable amount of hydrocarbon in the form of bitumen, which if not removed earlier, decomposes in the sulphur furnace to produce moisture, which is then carried forward to the entire plant. This suggests that a molten sulphur filter is mandatory wherever black sulphur has to be utilized. Under Indian conditions where the supply of sulphur is uncertain, it may hence be advisable to make a provision for both the molten sulphur filter as well as the hot gas filter in the plant design.

Process Selection: Though basically all the processes for the production of sulphuric acid are alike, there are many differences in the converter loop of different designers. The oxidation of sulphur dioxide takes place in 4 stages, with cooling of the gas between the stages. The different designs differ in the method of this inter-stage cooling, which can be effected in various alternate methods, such as (a) Indirect Heat Exchange, either with some process stream or with air. This preheated air can be used for sulphur combustion and thus improve the overall thermal efficiency of the plant. (b) Steam-raising or superheating in Waste Heat Boilers—This is generally done only for the I bed exit gases as the temperature conditions are most favourable here. (c) Cooling by quenching with cool, dried air.

A combination of these alternatives may be utilized, depending on the final product, capacity of the plant, plant economics and ease of operation. The four most common combinations are given in Figs. 1 to 4. Depending upon the process route selected the sizes of various equipment also change and so does the catalyst loading

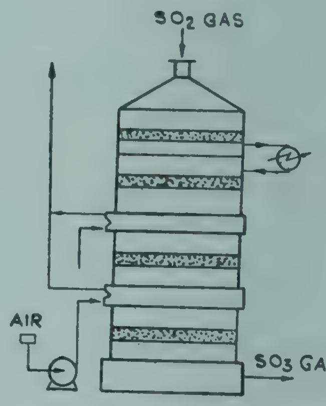

Fig. 1

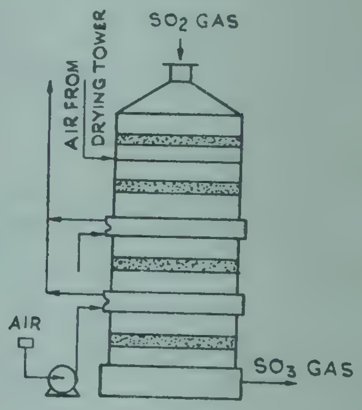

Fig. 2

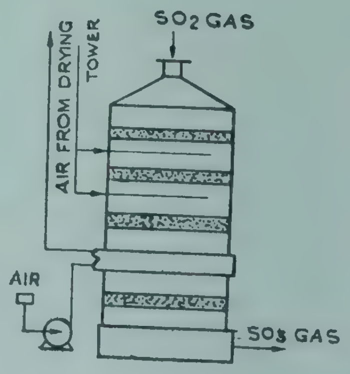

Fig. 3

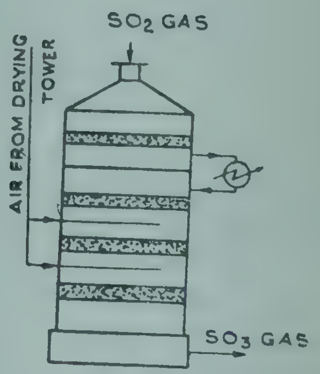

Fig. 4

as given below by M/s. Catalyst India Ltd.* for the 4 cases.

TABLE 1—CHANGES IN CATALYST LOADING

Sl. No.	Final Gas Strength (as % SO_2 inlet I bed)	Catalyst, l/te of 100% H_2SO_4 produced daily
1.	8.3	195
2.	7.8	216
3.	6.4	190
4.	7.3	216

In the case 1, the inter-stage cooling is done by Indirect Heat Exchange. The usual practice is to use a waste heat boiler after I bed, and internal heat-exchangers after II and III beds. In the case 2, cooling of I bed exit gases is effected by air quenching while indirect heat exchangers are used after II and III beds. Under case 3, cooling after I and II beds is by air quenching and indirect heat exchanger after III bed. Under alt. 4 a Waste Heat Boiler is used after I bed, while cooling after II and III beds is by air quenching.

The major equipment, which are affected by selecting one process route or another, are the main air blower, drying and absorption towers, heat exchangers, and the converter. In the Indian Context, the alternatives 2 and 3 appear more attractive propositions for medium-sized plants as in these cases the operation of the plant becomes much smoother due to the elimination of the high temperature heat exchangers. Cost analysis of the major equipment shows that the initial investment is slightly higher for case 3 than in case 2. However, case 3 provides higher by-product steam recovery, and the operation is also quite smooth. Variations of the cost for the major equipment for a 250 TPD plant are as given below (Table 2).

TABLE 2—VARIATIONS OF COST FOR THE MAJOR EQUIPMENT OF A 250 TPD PLANT

Sl. No.	Item	Increase (+) or Decrease (−) for Alt.2 as compared to Alt.3, 000Rs.
1.	Main Air Blower	− 87
2.	Drying and Absorption Tower	−140
3.	Heat Exchangers	+180
4.	Converter	−270
5.	Catalyst	+140
	Total:	−177

The extra steam generation under alternative 3 is 30 Te/day.

Similar results were obtained while comparing plants for a capacity of 500 TPD. It would thus be evident that case 3 is the best suited process route under the Indian conditions. However, the location of the plant and the final product concentration are other salient feature which have to be studied while a process route is selected. For instance, if the desired product is a 20 per cent oleum and the location a highly humid area, case 3 cannot be adopted as the moisture balance of the plant shall get upset due to the greater amount of water entering the system with atmospheric air.

With still higher capacities, say in the range of 1000 TPD plants, the overall economy is significantly improved by raising the steam production. Both the cases 1 and 4 provide greater steam as by-product. In case 4 the heat exchangers after 2nd and 3rd beds are avoided without much effect on the overall gas composition. Besides, it is also possible to replace the standard steaming type economiser after the 4th bed by a simple boiler feed water heater. As such, case 4 suggests itself to be the best process route in plants of higher capacities.

Cost Reduction

In any processing industry the possibility of cost reduction always exists. These economies should be planned in a manner such that the plant operation is not affected in the long run. Economies should be made in those areas where the cost is maximum. With this end in view, the cost analysis of a sulphuric acid plant has been made both for the equipment cost of various sections as well as for the overall plant costs. The salient results are as reproduced below (Table 3).

The foreign exchange involved is roughly 10-15 per cent of the overall plant cost, depending upon the type of particular plant. The bulk of the imported component is made up of vendor's equipment; instruments and valves are the other items which account for foreign exchange.

From the above it may be concluded that the design of the converter is critical from the techno-economic point of view. The Planning and Development Division of FCI Ltd. has developed the requisite know-how in the design of sulphuric acid plant and so far designed and engineered three plants which are at present under various stages of execution.

P & Division has also developed the know-how for the Double Catalyst Double Absorption process which is a practical translation of the Le Chattelier's principle.

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*They are the only manufacturers in India of this catalyst.

TABLE 3—Cost Analysis of a Sulphuric Acid Plant

(a) *Based on equipment cost*

Sl. No.	Section	% of Total Equipment Cost
1.	Sulphur Melting and Purification	5–7
2.	Sulphur Burning	4-5
3.	Waste Heat Recovery	20
4.	Gas Filtration	2
5.	Converter loop (including catalyst)	30-35
6.	Air Drying system (including Air Blower)	20
7.	Absorption system	15
	(b) *Based on overall plant cost*	
1.	Fabricated Equipment	30-35
2.	Vendor's equipment	8-10
3.	Brick-lining and tower packing	10-15
4.	Catalyst	4- 5
5.	Values, piping, insulation,	15-20
6.	Instrumentation	5-10
7.	Electricals	5
8.	Civil Works	10-15
9.	Erection	10-15

The conversion of sulphur dioxide to trioxide is effected in two stages. In the first stage, an overall 95-96 per cent conversion is attained in the first three beds of the converter. Sulphur trioxide is tapped from the converter, cooled and absorbed in a 98 per cent circulating sulphuric acid solution. The exit gases from the intermediate absorber are freed of the entrained mist and re-heated to the optimum temperature level for the II stage of conversion. The heat energy for reheating is obtained from the exothermic heat of oxidation of sulphur dioxide released from earlier and subsequent stages of conversion. Due to the removal of the sulphur trioxide from the gas stream, a more favourable equilibrium is established and in the II stage of oxidation an overall 99.7 per cent of sulphur dioxide conversion achieved. The gas from the II stage conversion is cooled and sulphur trioxide is absorbed in the final absorber. The resultant gases having very low amounts of sulphur dioxide and trioxide are vented to the atmosphere.

Soundness of design, simplicity of operation and minimum maintenance are the built-in characteristics of the plants designed by P & D Division. It may also be mentioned here that as far as the indigenous know-how is concerned, P & D Division is the only organization in this country to have developed these processes.

Converter Design

The design of the Catalyst Converter can be subdivided into the following sections: (a) Fixing the Converter diameter, (b) Catalyst loading and distribution, (c) Heat balance and design of Heat Exchangers and/or Air Quenching system, (d) selection of catalyst supports, (e) selection of materials, and (f) specification of external insulation. The above aspects are briefly discussed below:

(a) *Fixing the Converter Diameter:* This is done on the basis of two main criteria, viz. (i) The catalyst supplier provides a range of velocities from the point of view of the characteristics of the catalyst. M/s. C. I. L. recommend a range of 0.3—0.45 m/sec at 0°C and 1 atmosphere pressure. The designer has to limit his velocity accordingly; (ii) the allowable pressure drop in the system, which is a function of the type of the plant and the type of purification facilities incorporated in the design.

Once the velocity has been fixed the diameter can be readily calculated.

(b) *Catalyst Loading and Distribution*: This can be done by standard methods, provided the catalyst characteristics are know. However, this part is usually taken care of by the catalyst supplier as this affects the guaranteed performance of their catalyst.

(c) *Heat Balance & Design of Heat Exchangers:* The design of heat exchangers is done by the usual methods of heat transfer which are extensively covered in the chemical engineering literature.

Air quenching system designs are based on the experience of the designer. The main factor is that the cool air should be completely mixed with the hot gases from the earlier contact stage with such efficiency that a constant temperature is obtained and the composition is the same everywhere.

(d) *Selection of Catalyst Supports*: The two most common type of catalyst supports are (i) a bed of suitable material and (ii) plates with perforations, the latter giving lower pressure drop but is costlier. The plate is so designed that it provides the maximum possible free area to reduce the pressure drops. However, the design should be such that even after prolonged use when the catalyst has undergone attrition, the reduced size of pellets do not pass through the openings. As the minimum pellet size is important for the designer to ensure that the support is properly sized, he expects the catalyst supplier to maintain a certain size range and to ensure that the individual pellets will not be of size significantly different than that ordered for.

The other common support is a bed of quartz pebbles, which are usually 40—50 mm in height, size of individual pebbles being in the range of 12—25 mm. The pebble, as also the plate, should be chemically inert and such that it has no tendency to link bonds with the catalyst. An alternative to quartz is a similar bed of crushed fibre-bricks or other suitable refractory material.

(e) *Selection of Material:* The shell—in case it is not bricklined—is generally made in two sections. The zone, where the temperature is above 500°C, is made of a suitable heat-resisting material. The cooler zones are generally of boiler grade steel. For large converters some designers prefer to instal a central supporting column, usually made of grey cast iron or proprietary materials like Meehanite, etc. Supporting beams are usually made of high temperature alloy steel, though some designers also select stainless steel AISI-321 for the higher temperature zone. The nozzles, manholes and other openings are usually of boiler grade steel. The grate is made of grey cast iron or Meehanite.

In some installations, particularly those using air-quenching after the I and II beds of catalyst, the high temperature zone is brick-lined and the shell, even for these zones, is made of boiler grade steel. The purpose of brick-lining is to ensure a shell temperature low enough to be in the working range for boiler grade steel and also help to provide a higher gas velocity in the I bed, which is of significance in the design of the converter.

In the first bed the temperature being the maximum, selection of material is also critical. Some designers prefer aluminizing of the zone. Aluminizing helps withstand the high temperature, as also the corrosive atmosphere prevailing here.

(f) *External Insulation:* The proper insulation is a vital factor in the smooth and efficient operation of the contact converter. As the converters are sized optimally, it is important that the specified temperature conditions be maintained. The insulation thickness is so selected as to obtain a reasonable heat loss figure. M/s C. I. L. mention a figure of 200 k Cal/hr m^2.

The catalyst is screened to remove fines before being charged into the converter. The main precautions in the screening and handling of the vanadium catalyst are the avoidance of excessive handling, mechanical shocks and moisture, which are necessary to ensure a correct pellet size and a minimum amount of fines. Smaller pellets may not only pass through the supports, but will also increase the system pressure drop. Screening should also be completed in the shortest possible time, preferably in dry weather, so that there is no appreciable moisture take up by the pellets.

Pollution Problems

An important aspect in the sulphuric acid plant design is the control of atmospheric pollution.

Of late there has been an unprecedented awareness towards a cleaner atmosphere; all future plants shall have to be planned accordingly. The control of emissions can be categorized under the following 3 heads: (1) Reduction in the extent of emission of undesirable constituents of the gas; (2) recovery of the undesirable components; and (3) proper dispersion of the gas in the surrounding atmosphere.

Any of the above mentioned three methods can be selected depending upon the capacity and the location of the plant. Dispersion is the simplest of the three methods as all that is required is an adequately designed stack. Recovery can be either as sulphur dioxide which can be bottled or recycled, or else in the form of a by-product like Ammonium Sulphate. The precise method and process of recovery is dependent on the marketability of the product as also on the type of other plants at the particular location.

In cases where the SO_2 has to be recovered, the process route selection becomes further involved as the sizes of equipment in the recovery system will also have to be considered. Naturally a more concentrated gas shall be preferred which would rule out case 3 as the suitable process for the main plant design.

Of late greater attention and emphasis is being placed on the reduction of total emissions from the plants (route 1), as mentioned above. For the following 2 suitable alternatives available: (i) DC/DA Double Catalysis/Double Absorption system; and (ii) pressure process.

Recent Developments

While the DC/DA system has been adopted in many large capacity plants, the pressure process is a comparatively recent development and has great potentialities to displace the conventional processes as it has many distinct advantages over the atmospheric pressure processes. It is expected to effect the following savings: (i) savings in sizes of ducting and equipment; (ii) Lower heat transfer surfaces for boilers and heat exchangers; (iii) lower catalyst requirement; (iv) reduction in volume of sulphur trioxide absorber.

It has been reported that one such plant, engineered by M/s Krebs and Cie and based on the Kuhlmann's know-how, has been commissioned in France. It is rated to produce 575 tpd of acid at 4 atm. operating pressure but the details about its performance is not known.

Conclusion

Sulphuric acid technology has always kept abreast with the developments in the processing industry. It has a record of complete renovation in every two decades. The lead chamber processes, which were in operation for a long time, have been replaced by the contact process. In the latter case also the converter design has radically changed over the years. Thanks to the better understanding of the reaction mechanism and cybernetic tools like digital computers, the design has undergone a metamorphosis from the modest beginning with the Mannheim converters to the present day 4 bed system. Ecology dictated the advent of the DC/DA processes. If DC/DA processes rule the roost in the seventies, the eighties are likely to be dominated by the pressure processes.

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UDC 66·074·48 : 546·17

The different methods of treatment of nitrogenous effluents have been critically examined. Air-stripping is of scant use due to very high air-to-liquid ratio, calcium carbonate scale formation and nitrification in the stripping tower. Ion-exchange by synthetic cation-exchangers and ammonium selective natural zeolites is costly* and have operational difficulties, like resin-fouling and disposal of nitrogen-rich regenerant. Biological nitrification and denitrification is effective but involves the supply of organic carbon for the denitrification stage, which is a problem with nitrogenous fertilizer wastes normally deficient in organic carbon. Moreover, in this process nitrogen is lost to the atmosphere. In the method of treatment in algae pond, recovery of nitrogen of the waste as protein-rich algae, which can be processed for food and feed for livestock, may defray the cost of effluent treatment. Large area requirement for the shallow ponds may be a bottleneck. Adequate supply of carbon dioxide and its high loss may affect the economics. Land disposal is attractive where cheap forest or cultivated lands are available but overloading may pollute underground waters with nitrate nitrogen and deteriorate the physical properties of soil. The particular treatment to be adopted will depend on local circumstances, even if sacrificing the economics in the interest of protecting the ecosystem. But treatment methods, which can recover the costly nutrient as a saleable by-product, should be the ultimate choice.

Removal of Nitrogen from Nitrogenous Effluents

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The effluents of nitrogenous fertilizers industry contain a good amount of nitrogenous pollutants which find their way into the effluents from process leakages, floor washing, purging during shut-down and start-up periods and in abnormal plant operating conditions, etc. Of the nitrogenous pollutants, ammonia is by far the most toxic, its tolerance limit for inland surface water meant for pisciculture as given by ISI[1] is 1.2 mg/l as ammoniacal nitrogen. In the latest draft ISI standard[2], which is under circulation, a limit of 50 mg/l ammoniacal nitrogen has been suggested for nitrogenous effluents discharges to inland surface water. It is known that free ammonia (unionized ammonia) as exist at pH values above 7 is more toxic than the combined (ionized) ammonia, i. e. the ammonium ion. Natarajan[3] studied the toxicity of ammonia to marine diatoms and observed that free ammonia concentrations above 1.1 mg/l is toxic, concentrations around 55 mg/l inhibits photosynthetic carbon fixation by 90 per cent and concentrations around 275 mg/l stopped photosynthesis completely.

Tolerance limits for nitrate are higher, 20 mg/l being the permissive and 50 mg/l (11 mg NO_3-N/1) being the excessive limit in drinking water as specified by the Ministry of Health, Government of India[4]. Nitrate at higher concentrations is known to cause methemoglobinemia in infants[5], since the gastric juices of infants under six months of age have low acidity (pH $\geqslant 4$), nitrate-reducing bacteria can thrive in the upper intestinal tract, reducing nitrate to nitrite. Nitrite is absorbed in the bloodstream producing changes in hemoglobin converting homoglobin to methemoglobin which cannot carry oxygen, thus causing suffocation and giving rise to discoloration of skin[6]. Cyanosis in livestock, similar in most respects to methemoglobinemia in infants, had also been reported[7].

No tolerance limit has been fixed for urea and fish can tolerate urea to some extent[8]. However, under anaerobic conditions urea may prove to be as toxic as ammonia due to its hydrolysis to ammonia and carbon dioxide, the toxicity being due to the ammonia formed. Urea is also readily hydrolyzed to ammonia by the enzyme urease and by the bacteria of the *genus proteus*, more specifically

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*unless ammonia is recovered.

P. Vulgari, P. Mirabilis, P. Pseudovalerei, P. Americanas, P. Ammoniae and *P. Marganii.*

Another nitrogenous compound of importance in recent days from the pollution point of view is monoethanolamine (MEA), which is being increasingly used in fertilizer industries for scrubbing carbon dioxide. Gillette *et al*[9] found that MEA is toxic to fish at concentrations above 10 mg/l. Chakrabarty *et al*[10] found that micro-organisms in biological treatment can be acclimatized to tolerate MEA upto 30 mg/l. BOD contribution of MEA is 0.80−1.10 lb/lb MEA[11].

Apart from exerting to aquatic organisms, livestocks and human beings, nitrogen in various forms may pollute waters by causing eutrophication of receiving waters which might result in excessive algal bloom causing various nuisances.

The exact amount of pollution load in terms of nitrogen of a nitrogenous industrial effluent is difficult to predict as this would depend on various factors, such as plant capacity, type of the finished product, feedstock utilized, manufacturing process adopted and last but not the least on good housekeeping. However, it may be assumed that a modern nitrogenous fertilizer factory manufacturing 600 te/day of ammonia and 1000 te/day of urea would discharge about 4-6 mgd of waste water containing 4-5 te/day of urea and 1.0-2.0 te/day of ammonia. Old modelled plants may throw many times more nitrogen load on effluent than this figure. Uncontrolled discharge of nitrogenous effluents would pollute the receiving waters in various ways already mentioned necessitating some sort of control on nitrogen discharge by adequate treatment of the effluent.

Methods of Treatment

It can be said that pollutants are pollutants only when they contaminate the environment beyond the factory premises. Otherwise these are either valuable end-products or intermediates or even the raw materials for some processes. Thus, there are two ways of effluent treatment, viz. (a) material conservation or recovery process, and (b) non-recovery process.

In the first process valuable raw materials and products, otherwise lost to the industry, are recovered. Also the day is not too far, when the industrial growth will be inhibited by limitations of water resources unless reuse of water is planned. Material conservation process will also permit reuse of water, thus reducing the raw water requirements of the industries. The choice between these two ways so far has been made only from economy point of view as reuse of water is yet to be mandatory.

Direct recovery methods for nitrogen from wastes so far have not been economical. Indirect recovery in the form of protein-rich algae by utilizing the nitrogenous effluents as culture medium in suitably designed algae pond seems to be an attractive proposition. Nitrification followed by denitrification would efficiently remove nitrogen load but in this process the costly nutrient is lost to the atmosphere and not recovered. Physical-chemical methods, like air- or steam-stripping and ion-exchange have also been used to remove/recover ammoniacal nitrogen with varied amount of success.

Treatment in Algae Pond

Bhattacharyya *et al*[12] had made a comprehensive review on algae in waste treatment upto 1965. In their experiment[13] on removal of ammoniacal nitrogen from nitrogenous effluents, they observed that as high as 500 mg/l ammoniacal nitrogen did not inhibit algal growth and nitrogen metabolism. pH in all the experiments was maintained at 6.3±0.3, incidentally by bubbling carbondioxide, which obviously ensures the absence of unionized ammonia. Algal concentration was found as optical density photometrically at 600 mμ. Alkalinity loss due to generation of acid by utilization of ammoniacal nitrogen from ammonium salt was compensated by the addition of calcium carbonate or soda ash. Phosphate addition as dipotassium hydrogenphosphate (K_2HPO_4) was more effective than as sodium phosphate or as superphosphate. Addition of 20 per cent carbon dioxide gas was found more effective than 80 per cent gas. They also observed auto-flocculation when pH came down to 4.5-5.0 by alkalinity loss due to reason stated earlier and if not compensated by a base. Auto-flocculation became distinct at pH range of 4.0-4.2. Substituting carbon dioxide gas by a soluble organic substrate, e.g. glucose, and bacteria seed in the form of sewage showed higher growth rate. A growth rate of 250 mg./l./day was observed with glucose, whereas that with carbon dioxide was 162 mg/l/day. The predominant algal species in their[12] experiment was *Chlorella pyrenoidosa*.

In their later semi-continuous laboratory studies[14], 8 per cent carbon dioxide gas in air was bubbled through the culture at the rate of 170-200 ml/min. for 8 hours during the day time.

The above experiments were done with ammonium salts and pH of the culture was maintained around 6.3. Golueke *et al*[15] studied the effect of addition of nitrogen in the form of anhydrous ammonia, urea and sodium nitrate on algal growth in sewage treatment ponds. Though no mention has been made of the pH values reached, these must have been on the alkaline side. The culture was predominantly of *Scenedesmus spp.* constituting about 99.5 per cent in September and October. *Chlorella* increased from October and reached about 2 per cent in December. They[15] determined algal concentration in the culture by using a Whipple haemocytometer. When the ammoniacal nitrogen exceeded 45 mg/l algal production dropped to half of that at 20 to 30 mg/l and the colour turned to yellowish-green. At 55 mg/l concentration, the colour change became more pronounced and the culture would not survive long. Golueke, in his earlier studies, however observed that by increasing algal concentration in such cases so that nitrogen level does not exceed 40 mg/l at any time due to ready utilization by algae the culture can survive the otherwise toxic conditions. The above inhibitory effect was due to toxicity of unionized ammonia. Syrett[16] mentioned about a good growth of *Chlorella* and *Scenedesmus* in 0.01 M (140 mg $NH_4-N/1$) ammonium salts. Using a synthetic growth medium with ammonium nitrogen concentration of 116 mg/l, culture depth 12.5 cm, incident day light intensity 200-7,000 ft. candles (day average being 3076 ft. candles approx.), temperature 22-30°C, pH 6.3+0.3 and growth period of 6 days, Bhattacharyya *et al*[13] reported the ammonium nitrogen utilization rate and algal growth rate as 17.3 and 156 mg/l/day respectively. Varying the ammonium nitrogen level from 100 to 500 mg/l. in the above medium, they found that even as high as 500 mg/l of ammonium nitrogen did not inhibit algal growth or nitrogen metabolism. Using different ammonium salts in their synthetic effluent samples, they found that the growth rates of algae in ammonium chloride, ammonium sulphate and ammonium carbonate were more or less the same, i. e. around 167 mg/l/day, but ammonium nitrate in growth medium showed the lowest rate, i.e. 116 mg/l/day. In general, the average rate of nitrogen removal was roughly one-tenth of the average rate of algal growth. In their semi-continuous studies[14], rates of nitrogen removal and algal growth were 29 and 243-322 mg/l/day of algal solids respectively. These values were almost double of those obtained in their earlier batch studies.

Golueke stated that toxicity of urea at higher doses was slowly manifested as algae took up only a limited portion of urea nitrogen directly and the greater part must get hydrolyzed to ammonia by bacterial and enzymatic activity before the uptake. Syrett[16] stated that urea was probably the best nitrogen source for *Chlorella* as it did not encourage bacterial contamination, and did not change pH. *Urease* was not found in *Chlorella* and therefore it was suggested that urea was taken up directly without hydrolysis to ammonia, the mechanism is probably a combination of urea with ornithine to form arginine, which by the reverse reaction will regenerate the urea in the cell tissue, and one nitrogen of this urea will join aspartic acid and the other form ammonia. However, there are evidences using C^{14} tracer that urea breaks up before assimilation. Bhattacharyya *et al*[17] found algae culture in urea plant effluents in shallow outdoor tanks, a promising method for removal of urea nitrogen, provided other algal nutrients were supplemented in these media in correct proportions. While the growth of *Chlorella pyrenoidosa* was not effected appreciably upto 1100 mg/l. ammoniacal nitrogen, the tolerance for urea nitrogen was found to be about 5000 mg/l, the pH being maintained at 6.0-6.5 by bubbling carbon dioxide-enriched air. The average algal growth rate was 150-200 mg/l/day corresponding to 15-20 mg/l/day of urea nitrogen removal. It was found that removal of 1 g of nitrogen by algae required about 200-250 litres of 10 per cent carbon dioxide showing a loss of 50-60 per cent of the carbon dioxide applied.

The toxic effect of nitrate nitrogen on algal culture was seen at concentrations of about 30 mg/l, which became fatal at a concentration of 65 mg/l[15].

The optimum concentration of carbon dioxide for culture of Chlorella was 5 per cent in the atmosphere[18], and saturation light intensity of *Chlorella* was 600 ft./candles[19]. Additional light intensities were not utilized.

McKinney[20] reported about researches in the University of Kansas and Mississipi State University on the activated algae process, which might be feasible like the activated sludge systems.

Algae culture on nitrogenous effluents is attractive as the proceeds from the protein-rich algal production may defray the cost of effluent treatment. The limitation of this process is the supply of adequate carbon. In cases where waste flue gases, after proper scrubbing, could be used as a source of carbon dioxide, the economics would be more favourable. Carbon dioxide may also be obtained as a by-product from calcination of water treatment plant sludge or from lime kiln. Organic wastes from distillery, sugar factory, paper mills or food processing plants, containing high BOD, may also serve as an inexpensive source of carbon in case of combined treatment in oxidation ponds.

Golueke *et al*[15] and Bhattacharyya *et al*[13] studied the different methods of harvesting algae by centrifugation, flocculation with reagents and auto-flocculation, etc. Separation by cation-exchange resins is only of academic interest as it not economically feasible. Before discussing flocculation, it is desirable to know the electrokinetic behaviour of algal suspensions. Cell wall of *Chlorella* has the following compositions:

Protein	27 per cent (approx.)
Lipid	9.2
α-Cellulose	15.4
Hemicellulose	31.0
Glucosamine	3.3
Ash (containing iron and calcium)	5.2

High concentrations of protein (isoelectric point around pH 4) and of cellulose (isoelectric point around pH 2.5) may control the flocculation process[21]. Golueke observed that algae washed and suspended in distilled water flocculated when pH was lowered to 3, but not so in the original culture. Ives[21] observed a minimum charge in algae at pH of 7 to 8. From electrophoretic mobility studies of *Chlorella* cultures in the pH range of 2-10 and extrapolating values, it was observed that mobility should approach zero at a pH of 1[21]. It was also found at pH values above 10.5 algal particles flocculate irreversibly, possibly, due to lysis of the cells.

Of the different flocculants, alum is effective in the pH range of 6 to 7. Lime as flocculant has been found to be more efficient than alum at pH preferably above 10.5[22,23].

As mentioned earlier, Bhattacharyya *et al*[13] observed the phenomenon of auto-flocculation and the corresponding pH drop in the culture. Golueke *et al*[24] also mentions the phenomenon of auto-flocculation, but in their case supply of carbon dioxide was not external as their stabilization ponds treated sewage by symbiotic culture of green algae and bacteria and also pH drop due to liberation of free acid did not arise as they did not use ammonium salts of strong acids. They stated the conditions for auto-flocculation as an actively photosynthesizing shallow culture, relatively warm day and bright sunlight and probably the high pH levels attained on a sunny day[25].

Van Vuuren *et al*[26] stated that flotation was a simple and economical technique for the removal of algae. Levin *et al*[27] studied the froth flotation process for economically harvesting algae, clarification of algae from oxidation pond effluent and reclamation of algae in oxidation ponds for economic use. Clarification was achieved by adjusting the pH to 3 to 12 with choice depending on the economics and then removing the froth of algae. In the process of flotation, water containing flotable materials and solids with sp. gr. of very close to water, was saturated with air at a pressure of above 2 kg/cm², usually 3 to 4 kg/cm² and the pressurized water was released to atmospheric pressure in flotation chambers. Alternatively, the water was brought under vacuum and air bubbles from realeased air caused the flotation. The floated suspended matter, caused by minute air bubbles, was skimmed off. Vrablic[28] stated that air bubbles of size range of 30 to 120 microns were attached to the floc by entrapment, adsorption, collision or condensation and the particles obeyed Stoke's law.

From the above discussions, it can be said that auto-flocculation on a sunny day supplemented by lime/alum flocculation in adverse weather conditions should be ideal for the initial concentration step. However, use of cationic polyelectrolytes with alum had also been suggested[29]. This would reduce the aluminium content in algae should alum be used for flocculation. Cationic polyelectrolytes alone had also been used for algae flocculation but offered no economic advantage. Increase in molecular weight of cationic polyethyleneimine from 800 to 2000 increased its flocculation efficiency[30]. However, the toxicity of the most cationic polyelectrolytes is also to be considered. Following the initial concentration step, dewatering may be done in a solid bowl centrifuge or industrial type gravity filter. The final step of dehydration may be done in rotary drums. The main obstacles to this method of treatment are the requirement of large areas for the culture ponds, high carbon requirement and expensive method of harvesting and processing of algae.

2. Biochemical Nitrification and Denitrification

A century ago (in 1873) it was shown by Muller that formation of nitrate in soils, which occurs within 5 to 55°C, optimum being 37°C and in the absence of antiseptics is a biological process[30]. High organic matter and high alkalinity were known to inhibit this process though some base should be present to combine with the nitrous and nitric acids formed. Ammonium salts of strong acids do not nitrify without a base, the function of the base, like calcium or magnesium carbonate, is to form ammonium carbonate by double decomposition before nitrification can occur. In 1882 nitrogen loss in soil was observed and two types bacteria responsible for this were isolated. It was observed that reduction of nitrate, which occurs under anaerobic conditions and in presence of organic matter, stopped in presence of oxygen as the organisms need not reduce nitrate to obtain oxygen.

However, it was not until the observation of loss of nitrogen in the activated sludge process and the rise of sludge in the final settling tanks by bubbles of nitrogen gas formed by denitrification during the 1930s, that any attempt was made to utilize this process to remove nitrogen from waste waters.

It is known that five *genera* of autotrophic nitrifying bacteria, viz. *Nitrosomonas, Nitrococcus, Nitrosospira, Nitrocystis* and *Nitrosoglea*, of which the first being the most common, oxidize ammonia to nitrite by the following energy-yielding reaction:

$$(NH_4)^+ + 1\tfrac{1}{2}\ O_2 \rightarrow 2H^+ + H_2O + (NO_2)^- \qquad (1)$$

The optimum pH conditions varied from 7.2 to 7.8. The energy of this reaction enables the bacteria to fix carbon from carbon dioxide of air or carbonates. 35 parts of nitrogen being oxidized for every part of carbon fixed.

Bacteria of nitrobacter and nitrocystis oxidize the nitrite to nitrate according to the energy yielding reaction:

$$(NO_2)^- + \tfrac{1}{2}O_2 \rightarrow (NO_3)^- \qquad (2)$$

During the nitrification process, a part of nitrogen is converted to bacterial protoplasm of formula $C_5\ H_7O_2N$ according to the equation[31]

$$5\ CO_2 + NH_4{}^+ + 2H_2O \rightarrow C_5H_7O_2N + 5\ O_2 + H^+ \qquad (3)$$

Thus, on combining with equation (3), equations (1) and (2) can be written as given in equations (4) and (5) respectively:

$$55\ NH_4{}^+ + 5\ CO_2 + 76\ O_2 \rightarrow C_5H_7O_2N + 54\ NO_2{}^- + 52\ H_2O + 109H^+ \qquad (4)$$

$$400\ NO_2{}^- + 5\ CO_2 + NH_4{}^+ + 195\ O_2 + 2H_2O \rightarrow C_5H_7O_2N + 400\ NO_3{}^+H^+ \qquad (5)$$

When the environment is changed at this stage to anaerobic and the denitrifying bacteria is allowed to work, the nitrate is reduced to nitrogen gas according to reaction[32].

$$\begin{aligned} HNO_3 + 2H &\rightarrow HNO_2 + H_2O \\ HNO_2 + 2H &\rightarrow HNO + H_2O \\ HNO + HNO &\rightarrow H_2N_2O_2 \\ H_2N_2O_2 + 2H &\rightarrow N_2 + 2H_2O \end{aligned} \qquad (6)$$

A non-nitrogenous source of food should be available during the denitrification step. This, an organic substance, will be the energy source for the organism and will be oxidized under anaerobic conditions using nitrites and nitrates as terminal electron acceptors. Of the various organic electron donors (hydrogen donor as shown in equation 6) studied, viz. sucrose, acetic acid, ethanol, acetone and methanol, the last named is the best and least expensive[32–34]. Methanol requirement is given by the equation:

$$\text{Methanol, lb/day} = 2.47\ \text{lb}NO_3{-}N + 1.53\ \text{lb}\ NO_2{-}N + 0.87\ \text{lb D.O.} \qquad (7)$$

3.0 to 4.0 pound of methanol per pound of nitrate nitrogen are required to react with all the dissolved oxygen (D.O.) and to reduce nitrate to nitrogen gas[35,36].

Bringman[37] in his studies used crude sewage as hydrogen donors where the proportion of crude sewage to the nitrified sludge was automatically controlled by redox-potential measurement and the final effluent was aerated to remove any organic matter. About 20 per cent by-pass of sewage is considered satisfactory. Requirement of organic carbon is about 2.86 lb BOD per lb. of nitrate nitrogen. However, the disadvantage was that all the sewage did not pass through the nitrification stage resulting in incomplete nitrogen removal. Denitrification is slowed below pH 6 and nitrous oxide is the main product. pH should not go beyond 4.5 to 10 range, in fact 7.0 to 7.5 gives the optimum results[38]. Apart from the bases required to neutralize the nitrous and nitric acids produced by the oxidation of ammonia (about 2 moles of hydrogen are produced per mole of ammonium nitrogen oxidized), nitrifying bacteria require free oxygen, and nutrients specially phosphates, magnesium and iron. Organic compounds need not be present for the nitrification, in fact they might inhibit nitrification. Downing *et al*[39] concluded that the growth of *Nitrobacter* and *Nitrosomonas* and hence the rate of oxidation reactions of ammonia to nitrite and nitrite to nitrate is more in mineral solution than in waste treatment plants. The generation time, i. e. the time taken by a culture to double its number of bacteria of nitrosomonas is 0.33 to 2 days and 2.9 to 30 days in mineral solutions and waste treatment plants respectively. Heavy metals above certain concentration also inhibit nitrification, e. g. $Ni > 10$ ppm, $Hg > 2$ ppm and $Ag > 0.33$ ppm, etc.

Johnson *et al*[40] studied this method for removal of nitrogen from sewage containing around 25 mg/l ammonia nitrogen. Das *et al*[41] have worked with fertilizer factory effluents and observed that 40 hours of aeration was required for nitrification of 1000 to 2000 mg/l. of ammoniacal nitrogen. Higher nitrogen concentrations inhibited the microbial activity. At this stage, mainly nitrite is present and more time would be needed to oxidize this to nitrate. As the step of oxidation of nitrite to nitrate will only increase the time required for denitrification as can be seen from equation (6), they started denitrification at the nitrite stage itself. The minimum sucrose concentration required here was found to be 0.2 per cent. About 20 hours were needed in the denitrification step while using optimum ammonia concentrations. Development of nitrifying and denitrifying cultures were also discussed.

Most workers agree on the use of modified activated sludge aeration step for continuous nitrification, complete nitrification being achieved under steady conditions when the sludge age or the sludge residence time (i.e. the weight of sludge in the aeration unit divided by the weight of surplus sludge produced daily) is greater than the generation time (or the reciprocal of the growth rate constant, which is given by the number of generations per unit time) for nitrosomonas in mixture of waste water and activated sludge at the operating temperature. Recently,[31,42] a submerged film type of reactor with more retention time has been shown to be more efficient than an activated sludge or trickling filter plant. Wuhrmann[43] in his studies used an additional basin placed between the aeration tank and the final clarifier. The mixed liquor after aeration was retained in the basin and the activated sludge was kept suspended by stirring. Dissolved oxygen concentration is determined with a D.O. meter. Absence of oxygen indicated necessity of more oxygen supply or replacement of diffusers and concentration of oxygen above 2 ppm generally meant excessive oxygen and wastage of power by compressors apart from sludge bulking and sludge carry-over. Aeration step was the nitrification step, whereas denitrification occurred in the mixing basin. Percolating filters (trickling or sprinkling filter, also called biofilter) had also been used for nitrification. Traditional percolating filters were rectangular or circular shaped, about 6 feet deep, filled with broken stones, etc. of about 2 in grade, were built up on impervious floor and provided with underdrains. The effluent was distributed over the surface of the filter intermittently. Any detached film known as humus sludge, was retained in a humus tank. Modern use of plastic packings, though expensive, permits taller filters, greater voidage and reduced ponding. In spite of the low operating costs, less attention required and ability to nitrify strong industrial wastes, some of the disadvantages compared to the activated sludge process are high initial cost, larger area requirement and ponding during winter[44]. Optimization of the activated sludge process and its developments, i.e. the contact stabilization, where aludge is aerated upto 24 hours before contacting waste water and the main stream of waste water is aerated for 30 min. and the extended aeration process, where aeration period of 24 hours is employed are discussed in literature[32,45,46]. For denitrification, recent work suggests the use of a packed column of activated carbon[52] or an 1 in. gravel filter medium; the latter is suggested for removal of nitrate from drinking water[33]. During passage through the activated carbon bed, aerobic bacteria are effective till the oxygen supply is exhausted, and then under anaerobic conditions denitrification occurs in presence of an organic substance, like methanol. Before this biochemical nitrification and denitrification process can be actually utilized, pilot plant studies under actual conditions will be required. Very recently, DuPont[47] of Canada have installed the World's first denitrification plant at their Maitland Chemical and Fibres Manufacturing Complex near Brochville (Ontario) but further details are not available. The biggest drawback of this method is the supply of adequate organic carbon at the denitrification stage and loss of the costly nutrient to the atmosphere as nitrogen gas.

3. Ion-Exchange Method

Ion-exchangers, used for many years in water treatment for removal of cations and anions, are classified by the charge of the exchangeable ion. Thus, acid or cationic resins will exchange cations and base or anionic resin will exchange anions. A general purpose resin will exchange any of the common ions, but in a mixture of ions selectivity will occur. For strong cation-exchanger the order of selectivity is $Ca^+ < K^+ < NH_4^+ < Na^+$; for weak anion-exchanger the order is $SO_4^{2-} < HPO_4^{2-} < NO_3^- < Cl^-$. Thus, the ammonium ion can be removed by contact with a cation-exchange resin and nitrate ion can be removed by contact with an anion-exchange resin.

However, problems of fouling the resin with dissolved organics or suspended solids or other trace elements and disposal of regenerated waste water containing high ammonia concentration make the feasibility of this process questionable. Calcium and other cations present in the effluent may utilize the resin capacity before adequate removal of ammonium ion can take place.

Rohlich[48] reported on synthetic ion-exchange resin for removal of ammonia as well as other pollutants. Despite the apparent success of this method, the non-selective nature of the conventional ion-exchangers, which prefer calcium ions to ammonium makes the cost of this process prohibitive. The present authors also felt that if conventional ion-exchangers were used for ammonia removal excessive reagent wastes would be encountered.

Mercer *et al*[49] developed an ammonium selective ion-exchanger to remove ammonia from waste water using a natural zeolite, clinoptilolite which is selective for ammonium ions in presence of sodium, magnesium and calcium ions. Its saturation capacity is 1.61 ± 0.01 mg/l and empirical formula[50]:

$$(Na_2O)_{0\cdot70}\ (CaO)_{0\cdot10}\ (K_2O)_{0\cdot15}\ (MgO)_{0\cdot05}$$
$$(Al_2O_3)_{8\cdot5-10\cdot5}\ SiO_2,\ 6-7H_2O$$

Exhausted clinoptilolite is regenerated with solutions or slurries of lime. Ammonia is removed from the regenerant by air-stripping and exhausted to the atmosphere. High ratio of stripping air-to-ammonia-rich regenerant (of the order of 300 cu ft of air per U. S. Gallon of regenerant) dilutes the ammonia content of air such that air pollution is not a problem. The spent regenerant is fortified with more lime and recycled to the zeolite bed to remove more ammonia. As the regenerant is recycled, no liquid waste is generated. The main limitation to the wide applicability of this method is that this zeolite is found in USA only. Another disadvantage is the necessity of clarifying the effluents before feeding to the ion-exchange columns to avoid resin-fouling.

Barth[51] explained that the use of clinoptilolite has shown favourable efficiencies for removal of ammonia from secondary effluent during large pilot plant demonstrations. But limited data are only available on exchange capacity of various lots of the natural material, effect of trace elements on resin-fouling, attrition loss of the resin column and general operating costs. The biggest factor to be resolved in this process is the disposal of concentrated brine with very high ammonia content that results from the regeneration of clinoptilolite.

Cousins *et al*[52] reported recently on their pilot plant studies for the removal of ammonia from biodegraded weak ammonia liquor of a steel factory by ion-exchange using a sulphonated styrene divinylbenzene copolymer resin in the hydrogen form. Ammonia removals in their experiments ranged from 95 to 98 per cent from a level of 1250 mg/l to 60 to 12 mg/l in the effluent. Biological solids, coagulated in the ion-exchange beds, were completely backwashed out and no resin fouling was reported. Total backwash water used was about 40 U.S. gal/ft^3 (5.34 1/1)* of resin. Typical ion-exchange feed contained 1200-1300 mg/l ammonia, 2 to 15 mg/l CN and 30 to 250 mg/l SCN. In addition to removing ammonia, the ion-exchange units served to coagulate suspended solids and colloidal debris to reduce effluent colour from dark brown to pale yellow and remove thiocyanate from the waste. Thiocyanate removal claimed was 90 per cent. But from cost estimation of a full-scale plant of capacity 1500 m_3/day they came to the conclusion that the process would be uneconomical in terms of recovery of ammonia nitrogen.

Srivastava *et al*[53] investigated an ion-exchange process of ammonia recovery from coke oven weak ammonia liquor using a cation-exchange resin Sindex-C 26, prepared from a coke oven waste product. They obtained ammonia recovery of over 99 per cent and reduction of ammonia in the liquor from 1.025 to about 0.002 g/100 ml. by passing the liquor through the resin in its hydrogen form in the upward direction with simultaneous escape of acid gases like carbon dioxide, hydrogen sulphide and hydrocyanic acid from the top of the column. The liquor was earlier passed through a filter containing sand and coke to remove suspended oily and tarry matters. The adsorbed ammonia was reclaimed by regenerating the resin with about 20 per cent sulphuric acid, in the form of 12-14 per cent ammonium sulphate solution. 100 per cent ammonia recovery was obtained with acid consumption of about 2 per cent higher than theoretical. The steam required for getting ammonium sulphate from the solution in multiple effect evaporators is much less than that required by steam stripping or distillation. Corrosion is reduced due to operation at cold temperature and escape of acid gases before the evaporation stage. Good quality of effluent is obtained along with better finished products.

4. Air Stripping

Henry's law states that the mass of a gas adsorbed in a liquid at a particular temperature is proportional to its pressure. According to Dalton's law, the total pressure of a gas mixture is equal to the sum of the partial pressures each component would exert if it alone would occupy the same volume as the mixture of gases. From these two laws it is seen that under equilibrium conditions, the amount of a gas dissolved in water from a mixture of gases is proportional to its partial pressure, which is expressed as $C=H. P.$ (8)

Where C = concentration of soluble gas in liquid in unionised form (mg/l),
P = partial pressure of the soluble gas in gas phase (atm.), and
H = solubility coefficient (mg/l atm),
H depends on temperture.

Gases, like carbon dioxide and ammonia, deviate from Henty's law at ordinary temperature due to their reaction with water, but at higher temperature their combination with solvent decreases and deviation is less. Also as the temperature increases the partial pressure of water vapour (i.e. the vapour pressure of water) increases thus reducing the partial pressure of the gas over the solution. The true situation is that the gases escape from and dissolve in solution by the movement of the molecules of the gas and the solvent. In air-stripping, the air bubbles provide sufficient area while passing through, for diffusion of ammonia into the bubble and thus taking away the ammonia with it. For removal of ammonia from effluent by air-stripping, the pH of water must be on the alkaline side to assure that only unionized ammonia is present. Caustic soda is better than lime for raising the pH, possibly due to hindrance in mass transfer by high suspended matter concentration arising from the use of the latter[54]. On passing air through the solution, ammonia is taken away by lowering its vapour pressure to nearly zero. Kuhn at Wisconsin Uunversity, quoted by Rohlich[55,56] carried out studies on air-stripping to remove ammonia from sewage effluent using a tower packed with Reschig rings and observed that the optimum pH for stripping was 11.0. Only when pH is above 11, more than 95 percent of ammonia remains undissociated in solution, as the equilibrium of undissociated ammonia in water $NH_4^+ \rightleftharpoons NH_3 + H^+$ depends on pH as below:

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* 1m^3 = 35.414 ft^3 = 264 U.S. gallon

$$Pu=100[1-1/\ \{1+\text{antilog}_{10}\,(pH-p^{K}a)\}] \qquad (8)$$

Where Pu=percent of undissociated ammonia and $p^{K}a$=pH at Pu=50. $p^{K}a$ increases with decreasing temperature. It is about 9.4 at 20°C

With ½ in. Raschig rings in 7 ft column 8 in diam. and using 453 ft³ air per U. S. gallon of liquid (rather 453 ft³/min/gpm or 205 m³/min/1/sec) or an air-to-water ratio of 3500, he [55,56] could get 92.3 per cent removal of ammonia. Culp and Selechta[57] used packed tower and forced ventilation and found 80 per cent removal of ammonia at pH 9.3 and 98 per cent at pH 10.8 with air-to-water ratio of 8000. Culp[58] obtained 95 per cent removal of ammoniacal nitrogen using water loading of 2 gpm/ft³ and air supply of 400 ft³/U. S. gal (or 3000 m³ air/m³ effluent) at pH 11.5 in a 24 ft high tower with 1½″ × 2″ packings. Mckinney[59] stated that ammonia stripping method was impractical due to absorption of atmospheric carbon dioxide and consequent precipitation of carbonates and biological nitrification in the towers. A major cost item, not to be ignored, is the acid cleaning or mechanical scrubbing of scales formed on the tower packings. He also stated that ammonia is released in the air and is absorbed. Ammonia is readily soluble in air and will be returned to the water environment with no net gain.

Bayley, while discussing Rohlich's paper[55], has given a simplified equation. From Henry's law (eqn.8) and mass balance for undissociated ammonia, we have

$$V\frac{dc}{dt}=\rho Q\,\frac{C}{H}\text{—(10a); integrating (10a), }\frac{Q^{tR}}{V}=\frac{H}{\rho}\ln\frac{Cl}{C_2} \qquad (10b)$$

For continuously operating tower in which the effluent gas stream is in equilibrium with the concentrated liquid it can be shown that

$$\frac{C_1-C_2}{C_1}=\rho Q\ t_R/V.\ H. \qquad (10c)$$

H has been taken as 1.1×10^6 mg/lat 20°C)

The factor 10^3 in equation (10) is to convert ρ into mg/l atm. Thus, to calculate the volume of air required to bring about any specified reduction in concentration of ammonia in alkaline media in a continuous stripper we have the equation[55].

$$\frac{C_1+C_2}{C_1}=10^3\ PQ\ t_R/VH \qquad (10)$$

Where

C_1,C_2 = concentration of ammonia in the influent and effluent, mg/l.
ρ = density of ammonia vapour, g/l. atm.
Q = rate of flow of air, 1/hr
t_R = residence time in stripper unit, hr
V = volume of liquid in stripping unit, and
H = reciprocal of Henry's constant, mg/l. atm (assuming H to be independent of concentration)

Because of high solubility of ammonia, a large flow of air per unit flow of liquid is required, the cost of air compression per unit flow of liquid becomes considerable. Counter current stripping in packed towers is the most efficient form of stripping. Eliassen *et al*, quoted by Prabhakara Rao *et, al*[54], consider air-stripping to be the most economical method of removing ammoniacal nitrogen. The high air-to-water ratio requires the use of stripping towers with very low pressure drops essentially a water cooling type. Barth[51] has concluded that the use of high volume low pressure air stripping of ammonia from secondary effluent cannot be recommended for wide application in USA.

Because of the high cost of air-stripping Eliaseen[60] felt that it would not find wide application in the removal of ammoniacal nitrogen. Rohlich[55] also felt that the economics of the process was unfavourable. Baumann[61], however, reported that ammoniacal nitrogen removal as high as 90 per cent could be obtained by passing waste water through a closely packed aeration tower. This required waste water pH values above 9.0 and air flow rates of about 300 to 500 ft³/gal water. This process had been used successfully for stripping ammoniacal nitrogen from highly concentrated industrial waste stream. Kuhn[62] pointed out that almost no large scale plant data are available on the design, operation, performance and cost of air-stripping method for removal of ammoniacal nitrogen from waste water. The most severe bottleneck of air-stripping of ammoniacal nitrogen is high solubility of ammonia in water which is about 1000 times more soluble than carbon dioxide. Another difficulty brought about by high air requirement is poor performance at cold weather. The waste water is cooled by contact with air, thereby increasing the solubility of ammonia.

Recarbonation of the stripping plant effluent has been suggested to lower the pH from around 11 to eventually 7 to 8, before the effluent is discharged.

5. Steam Stripping

Steam stripping for removal of ammonia (i.e. steam distillation of ammonia from ammoniacal liquor in ammonia stills from coal carbonization wastes) is an established method. Lime is added to the liquor for removing combined ammonia. Here condensation of a part of steam heats the liquid, thereby decreasing the solubility of ammonia at high temperature, and the rest does the stripping.

6. Other Methods

Apart from the methods described above there are methods for removal of nitrogen from industrial wastes. These include demineralization by electrodialysis or reverse osmosis, breakpoint chlorination and land application, etc.

(a) *Electrodialysis:* This is a unit process that uses an induced electric current to separate the cationic and anionic components of a solution by means of selective membranes that permit ions to pass through the material from the diluted solution on one side to the concentrated solution at the other, the membranes being placed at right angles to the line of flow of the electric current. Electrodialysis is useful for partial demineralization of low mineralized waters with dissolved solid figures preferably below 2000 mg/1 such as municipal waste waters.

The problems associated with the electrodialysis process for waste water treatment include chemical precipitation of salts like calcium carbonate on membrane surface and clogging of the membrane by organics and similar colloidal impurities. Acid treatment followed by activated carbon pretreatment may be necessary to reduce membrane-fouling.

(b) *Reverse Osmosis:* This involves the squeezing out of water through cellulose acetate membranes against the natural osmotic pressures upto 750 psi (53 kg/cm^2) in order to accomplish separation of relatively pure water and ions. The mechanism involved in reverse osmosis include sieving, surface tension and hydrogen bonding by the cellulose acetate membrane. The flow of purified water, Q, is given by

Q = K. S. (pa-Po)
where K = a function of the material and fabrication process of the membrane.
S = Surface area of the membrane
pa = applied pressure, and
Po = Osmotic pressure (e. g. which for a brackish water containing 2000 ppm solids is 21 psi)

Reverse osmosis is normally a nonspecific process. More common cellulose acetate membranes have a longer life when pH of water is maintained at 5.0-6.0. At this pH range, ammoniacal nitrogen is present as ammonium ion and is retained by dense membranes, where nitrate and urea are poorly retained. It may not however reduce ammoniacal nitrogen to the permissible levels. Also this process yields an ammonia concentrated waste, which does not fully solve the problem.

Problems associated with desalination by reverse osmosis include concentration polarization, membrane fouling and passage of certain ions through the membrane. Concentration polarization is usually counteracted by designing reverse osmosis equipment to operate with high tangential velocities at membrane surfaces. By inserting sand and carbon filters, membrane fouling may be reduced.

(c) *Breakpoint Chlorination:* Basically this process consists of chlorinating nitrogenous waste water to oxidize ammonia to nitrogen gas and to reduce nitrate and nitrite to nitrogen gas. With molar Cl_2: NH_3 ratio upto 1.1 monochloramine and dichloramines are formed. With further addition of chlorine the chloramines gradually decompose and at molar ration Cl_2: NH_3 of 2:1 "Breakpoint" occurs showing negligible chloramine residuals if sufficient contact time is given. After 'Breakpoint' HOCl reamins in solution. Rate of oxidation of ammonia is optimum at pH 7-8.

$$2NH_3 + 2Cl_2 \rightarrow N_2 + 6HCl$$
$$4NH_2Cl + 3Cl_2 + H_2O \rightarrow N_2 + N_2O + 10HCl$$
$$2NHCl_2 + H_2O \rightarrow N_2O + 4HCl$$
$$HOCl + NHCl_2 + H_2O \rightarrow 2NO_2 + 5HCl$$

Possibly, nitrogen, nitrous oxide and NCl_3 are the possible gaseous products at "Breakpoint" chlorination.

Farrel[63] reported that up to 10 mg. of chlorine is required for 1 mg. of ammoniacal nitrogen and St. Amant and McCarty stated that each mg of nitrite nitrogen will exert a chlorine demand of 5.06 mg. Recent studies by Barth[51] with breakpoint chlorination have shown that essentially all the ammonia can be oxidized to nitrogen gas by proper control of pH to satisfactory levels by lime or caustic treatment.

The high chlorine demand is the biggest limiting factor for use of this process for the bulk removal of nitrogen from industrial wastes, but consideration can be given to use breakpoint chlorination of polishing operation.

(d) *Removal by Soil*: Soils are being considered extensively as disposal system for secondary effluents and other liquid wastes because the natural chemical and biological processes can be used for purification. Filtering waste water through soil removes most of the biodegradable material and faecal microorganisms. The removal of nitrogen and phosphorus may be as high as 90 per cent of the original content in secondary effluent. It has been found that the two most important factors that control the movement of nitrogen through soils are physical adsorption, chemical fixation, and biological action, the former phenomenon seems to play the major role in the removal of ammonium nitrogen by agricultural or forest lands and pitty soils. The ammonium ion adsorption ratio (AAR) can be used to estimate the percentage of the cation-exchange capacity (CEC) that can be occupied by NH_4^+ ions when the concentrations of ammonium and the principal competing divalent ions in the water filtering through the soil are known. The AAR is calculated as:

$$\frac{[NH_4^+]}{(\frac{1}{2}[Ca^{++}] + \frac{1}{2}\,[Mg^{++}])^{\frac{1}{2}}},$$

where concentrations are expressed in me/l.

The adsorbed NH_4^+ ion is not necessarily stable except in an anaerobic soil system because it can be oxidized biologically to nitrate when oxygen becomes available between irrigations and might pollute the ground water with respect to nitrate nitrogen.

Ammonium nitrogen may also be fixed and retained in the soil by becoming trapped in the intermicellar layers of clay minerals, such as montmorillonite and vermiculite, or by forming complexes with the organic fraction of soil, the latter phenomenon could account for the removal of considerable amount of ammonium nitrogen from waste water applied to land.

In the land disposal systems the amount of ammonium nitrogen removed by volatilization as ammonia gas is small, but a substantial amount of nitrogen could be removed during travel through a long stream or channel to the disposal area. Denitrification, bilogical or chemical, also accounts for some amount of ammonium nitrogen removal from nitrogenous effluents in a land disposal system. Assimilation by soil microbes also play some part in the removal of nitrogen.

But nitrogen removal by agricultural cropping is perhaps the most effective way to reduce the nitrogen content of an effluent because nitrogen is completely removed from the system when the crop is harvested. The best crops for such a system would be those with high nitrogen requirement such as Bermuda grass—a perennial grass with long growing season and tolerant to floods. The requirement of large areas of land is the major limitation of this process particularly in the vicinity of large urban areas, However, this process may be attractive in localities with ready availability of cheap land and economic return for the crop harvested. Other difficulties with this process are that under conditions of heavy loading with nutrient laden effluent, the physical conditions of the soil may deteriorate by pure clogging and contamination of ground water by nitrate nitrogen.

Summary

Various processes—physical, chemical and biological —for removal of nitrogen from nitrogenous waste waters have been reviewed. Of these, air- and steam-stripping at elevated pH, ion-exchange, biological nitrification-denitrification, algae culture and land disposal seem to have technical feasibility though these methods are not always economically viable at the present stage. Air-stripping of ammonia cannot yet be considered practical except in special circumstances because of the very high air to liquid ratio and associated problems of calcium carbonate precepitation and nitrification in the stripping tower. Ion-exchange by commercial synthetic cation-exchangers or ammonium selective zeolites have not yet been popular due to higher cost of ammonium sulphate thus recovered and other operational difficulties chief of which are resin-fouling by suspended solid and dissolved organics of the waste water, disposal of the nitrogen-rich concentrated brine solution. However in a tropical country like India air-stripping would not pose much problem as would occur in a cold country. Steam stripping and ion-exchange methods would be attractive for treating concentrated ammoniacal waste water, when these are properly segregated. Biological nitrification and denitrification can effectively remove nitrogen from waste waters but the supply of adequate organic carbon in the denitrification stage may be a problem with nitrogenous fertilizer wastes normally deficient in inorganic carbon. The cost of air supply in the nitrification stage is also to be considered. The nonrecovery of nutrient is another drawback of the process. Removal of nitrogen from nitrogenous wastes by culturing algae in a suitably designed algae pond utilizing the nitrogenous wastes as feed medium and carbon dioxide–enriched air as carbon source seems to be an attractive scheme at the present moment especially in tropical countries like India with abundance of sunshine and long summer days. Large area requirement for shallow tanks/ponds suitable for maximum light diffusion, however, may prove to be a bottleneck in the vicinity of large-population centres. Supply of adequate carbon dioxide to these ponds and high carbon dioxide loss may also stand in the way of economics of the process. However nitrogen of the waste is recoverable as protein-rich algae which can be processed for food and feed to livestocks. Land disposal is attractive where cheap forest or cultivated lands are available but for efficient removal of nitrogen some source of carbon has also to be supplied to the waste as the plant tissue has got a certain C:N ratio. Overloading may create underground water pollution problem by nitrate nitrogen and deteriorate the physical properties of soil.

It is therefore concluded that no standardised and economic method of nitrogen removal has yet been developed for commercial application. But as the costly nutrient may prove to be a pollutant and might degrade the environment to a substantial degree in case of uncontrolled discharge, some method should be adopted for its removal from waste waters irrespective of the economics of the process or the manufacturing processes changed so that the minimal amount of nitrogen only finds its way to the waste. Segregation of concentrated wastes and their separate treatment should be considered wherever possible.

The particular treatment to be adopted would depend on the local circumstances but treatment method which can recover the costly nutrient as saleable by-product should be the ultimate choice.

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[Original mss received on April 24, 1973
and resubmitted after revision on Oct. 15, 1973]

UDC 553-611: 631·4 (540)

The presence of different clay minerals in various groups of soils of India has been enumerated. It has been shown the dominant clay minerals in the alluvial soils are illite and kaolinite; in the black soils—montmorillonite and beidellite; in the red soils—kaolinite and illite; in laterite and lateritic soils—kaolinite and kaolin-like minerals; in mountain and hill soils—illite and kaolinite; in brown or grey-brown podsolic soils—hydrous mica and illite; in brown forest soils—illite and kaolinite; in desert soils—illite, chlorite, and attaphulgite; in saline and alkali soils—illite, chlorite, and attaphulgite; in saline and alkali soils—illite, kaolinite and chlorite; and in marshy and peaty soils—montmorillonite.

Clay Minerals in Different Groups of Soils of India and Factors Affecting Their Genesis

By R. D. Gupta* and S. P. Raychaudhuri*

The main purpose of this article is to present the nature and distribution of clay minerals in different groups of Indian soils with reference to factors responsible for their genesis. Clay minerals, which have been synthesized from residual products of weathering, are colloidal in nature, usually crystalline and are very important constituents of soils. They are hydrous aluminium silicates frequently mixed with some replacement of aluminium by iron and magnesium and are called the skeleton of the soils, as most of the physico-chemical, and morphological properties of soils are dependent upon them. The important clay minerals found in soils are illite, montmorillonite, halloysite, kaolinte, vermiculite, chlorite, nontronite, saponite, attaphulgite or palygorskite, sepiolite, etc.

Classification of the Important Soil Groups of India

Soils of India have been classified into the following groups: *Alluvial Soils:* These are present in parts of Rajasthan, Punjab, Uttar Pradesh, Bihar, W. Bengal, Assam, Orissa, Madhya Pradesh and Jammu and Kashmir.

About the presence of clay minerals in these soils there is a lot of controversy. For example, Roy[1] and Roy and Das[2] stated that the alluvial soils of Delhi contained illite as dominant mineral with small amount of montmorillonite, but Das[3] indicated the presence of small amount of kaolinite in addition to illite in the alluvial soils of Karnal and Delhi. According to Sharma[4], the transitional soils of alluvial origin belonging to Ambala, Hoshiarpur and Gurdaspur districts (Punjab) showed the presence of kaolinite mixed with hydrous mica and montmorillonite, while those of Ferozepur, Hissar, parts of Ambala, Jullundur, Amritsar, Karnal, Ludhiana and Patiala had montmorillonite as the dominant clay mineral. Illite with a fair amount of montmorillonite were recorded as the prominant clay minerals in the alluvial soil of Saharsa district (Bihar) by Sahay *et al.*[5]. Sen and Chatterjee[6] observed kaolinite in the premonsoon Gangetic silt while monsoon silt was rich in illite. Low-lying soils of the lower Gangetic plains of eastern Uttar Pradesh were dominant in illitic type of clays with fair amounts of montmorillonite[7–9], On the contrary, Sinha *et al*[10] showed the presence of montmorillonite with lower percentage of vermiculite in the alluvial soils of South Bihar. It was also supported by Chatterjee and Dhar[11] and Khanna *et al*[12]. According to Sarkar and Chatterjee[13], the alluvial soil clay predominated with illite and small amount of montmorillonite. Prasad *et al* [14,15] observed identical clay mineralogical composition in all the alluvial soils of Bihar, containing illite as the most predominant part followed by kaolinite with the exception of Patna and Sabour soils which had some chlorite also. Similar results were also obtained by Gupta[16] while studying the alluvial soils of Jammu and Kashmir. Gangetic alluvium soils of W. Bengal (Howrah, Burdwan, Hooghly, Murshidabad and Nadia) had illite as the dominant clay mineral[12]. All the alluvial, riverine, old soils from the western and central U. P. had been reported to have illite and chlorite as the main clay minerals by Gupta[9] and Chatterjee and Gupta[18], but the eastern region had montmorillonite as dominant part with small amount of illite and chlorite. According to Yadav *et al*[19], chlorite content was quite high in the top horizon of soil profile (alluvial plain in the north Ganges river) under bamboo and sisso plantation of Champaran district (Bihar). Illite was the predominant clay mineral in the six types of Aligarh (U. P.) soils with presence of some chlorite, laboradorite and calcite[20]. From the recent studies of Sehgal and Coninck[21], it appears that in addition to illite a dominant clay mineral —vermiculite and montmorillonite formed an important associate in clay mineral composition of Punjab soils. Apart from this, kaolinite was present, in minor to moderate amounts in the *Ustic* and *Udic* soil groups of Punjab. The real chlorite mineral was noticed in some *Udic* soil group (*Hapludults* and *Hapludalfs*) of Punjab.

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Black or Black Cotton Soils (*Regu*)*:* These are mainly found in Andhra, Madhya Pradesh, Maharashtra and Gujarat. Isolated patches are also found in parts of Tamil Nadu, Karnataka, Bihar and Uttar Pradesh.

Without controversy, it has been proved by many scientists that black or black cotton soils of India contained montmorillonite as the dominant clay mineral[17,22,35]. According to Singh[36] and Singh[37] the regur or black cotton soils were rich in montmorillonite and beidellite group of clay minerals. It was also the finding of Desai[38]. Das[3] reported montmorillonite with a fair amount of kaolinite and traces of illite in the black cotton soils of Indore. Recently, Kulkarni and Deshpande[39] observed the presence of montmorillonite and beidellite in the black soils of Karnataka.

Red Soils: They include red earth, red loam, yellow earth and brown earth, etc. They are chiefly confined to the whole of Tamil Nadu, Karnataka, South and East Bombay, East of Hyderabad, Madhya Pradesh, Orissa, Chotanagpur and Santhal Paraganas in Bihar, Birbhum in W. Bengal, Mirzapur, Jhansi and Hamirpur in U. P.

Raychaudhuri *et al*[22], Bagchi[40], Ghosh *et al*[41], and Sinha *et al*[42] pointed out kaolinite and halloysite as the prominent clay minerals in these soils. This was also supported by Kulkarni and Deshpande[39]. Krishnamurthi and Deb[93] reported that some red soils of Karnataka contained nontronite. In the words of Rudra[43] the red soils of Burdwan and Birbhum (W. Bengal) had kaolinite as the dominant fraction. On the other hand, Das and Das[44] found illite with lesser amount of kaolinite in red soils of Karnataka. It was also true in case of W. Bengal soils[45]. Raychaudhuri[46] was also of the same view. Kaolinite and illite had been observed by Mandal[47], and Sinha and Mandal[48], in the soils of Chotanagpur areas (Palamau, Singhbhum, Hazaribagh, Netarhat and Ranchi). Ghosh and Das[49] also arrived at the same conclusion while working on the red soils of Ranchi. The most of the sedentary soils (red, reddish, yellow or yellowish in colour) of Bihar had been found to contain kaolinite with fair amount of illite and small amount of chlorite[14]. Das and Das[50] pointed out that although the brown soils of Karnataka were dominated by montmorillonite but there was always present a small amount of illite. Montmorillonite was obtained by Sarkar and Chatterjee[13] in some red soils of India. Kaolinite was the dominant clay mineral in the red loam soils of Karnataka[51].

Laterite and Lateritic Soils: They are especially well developed on the summits of hills of Deccan, MP, the Rajmahal hills, Eastern Ghats, certain parts of Orissa, Assam, Karnataka, Malabar and Western Ghats.

These soils are characterized by the presence of Kaolinite or kaolin like minerals[52,43,33,53]. Basak[54] supported the above view by reporting the laterite soils of W. Bengal (Bankura, Midnapur, Burdwan and Birbhum) containing kaolinite as the predominant clay mineral. Yadav *et al*[55] came to the same concluson after studying the soils of Western Ghats under the ever green forests. Laterite soils of Mangalore (Karnataka), Alwaye (Kerala) were found to contain kaolinite and illite[41].

Mountain and Hill Soils: These soils are found in parts of Kashmir, Assam, U. P., W. Bengal, Himachal Pradesh and Bihar.

The mountain soils of Kashmir were reported to contain illite and kaolinite[56], whereas the hill soils of Assam (Cherrapunji) and foot hill terai soils of Uttar Pradesh contained illite, and illite with fair amount of chlorite and kaolinite respectively.

Brown or Grey Brown Podsolic Soils: They are found in Himachal Pradesh (Kulu, Kangra and Simla Hills), Uttar Pradesh (soils of Kumaon division), Jammu and Kashmir (Pahalgam), as reported by Taylor *et al*[57] Hoon[58], Sharma[4], Kaul[59] and Gupta[9].

The presence of hydrous mica and kaolinite was indicated by Sharma[4] in Kangra and Simla hill soils. It was also supported by Sharma and Rao[60], according to whom the apple-growing soils of Kotgarh (Himachal

Pradesh) contain hydrous mica throughout the soil profile. Kansal[61] showed the presence of illite in Palampur (Kangra) soils. According to Sharma[62], the profile samples of Palampur had the dominance of montmorillonite with a mixture of kaolinite. The presence of illite, chlorite and montmorillonite–illite mixed layers in Kangra and Kulu soils were reported by Singh[53]. Gupta[16] observed illite followed by chlorite in the soils of Pahalgam (Jammu and Kashmir.).

Brown Forest Soils: These are present in Uttar Pradesh, Himachal Pradesh and Jammu and Kashmir[63–67,58,26]. Illite was the dominant clay mineral with a small amount of kaolinite in H. P. soils[66]. Same type of finding was also made by Raychaudhuri[46]. Shukla *et al*[67], while studying the foot hill soils of the Himalayas (Dehra Dun), found illite followed by chlorite. Similar results had also been obtained by Gupta[16] after studying the soils of Jammu and Kashmir (Pampore and Batote).

Desert Soils: These soils occur under arid and semi-arid conditions and are present in Rajasthan, South Punjab and Haryana.

Illite and chlorite were the dominant clay minerals with small amounts of sepiolite and montmorillonite in the desert soils of Ferozepur, Gurgaon and Nilokheri[68,69]. The above finding was not inconsistent with those of Millot[70], and Grim[71], according to whom the sepiolite was the dominant clay fraction in the desert soils. Illite with a fair amount of attapulgite were the chief clay minerals in the desert soils of western Rajasthan[72], except one (highest rainfall region) which contained montmorillonite. That montmorillonite is the dominant clay mineral was also reported by Chatterjee and Dhar[11] in some desert soils of India. This finding was, however, not in favour of Elgabaly and Khadr[73], who isolated attapulgite as the dominant constituent followed by kaolinite from the desert soils of Cairo (Egypt), whereas the montmorillonite and hydrous mica were completely absent. According to Jagan Nath[74], the soils of Ajmer and Hanumangarh (Rajasthan) had illite as the dominant part with small amount of chlorite.

Saline and Alkali Soils: These soils are found extensively, especially in Bihar, Uttar Pradesh, Punjab, Haryana, Rajasthan, and Jammu and Kashmir.

Raychaudhuri[75] reported that illite and kaolinite were predominant in saline alkali soils of Lucknow, while illite along with some quantity of kaolinite occurred in Delhi. But according to Kanwar[56,68], the saline and alkali soils of Punjab contained illite with lesser amount of chlorite. It was also the finding of Gupta[16]. Raychaudhuri and Patel[76], while making a comparative study of some typical saline and alkali soils occurring in certain climatic regions in India, found a mixture of montmorillonite and illite in these soils.

Peaty and Marshy Soils: They are found in Travancore Cochin, coastal tracts of Orissa, North Bihar, Almora (U. P.) and Madras.

The study on the clay mineralogy of these soils is very limited. However, according to Rao[77] the clays of peaty soils contained montmorillonite as the dominant mineral.

Factors Including the Genesis of Clay Minerals: In soils clay minerals are not stationary but are always in dynamic position due to a large number of environmental factors, such as parent rocks, climate, topography, vegetation etc. But no arrangement of these factors controlling weathering processes in a general order of importance is possible since all these factors are closely interrelated and, therefore, their relative importance is not always the same. For example, Hosking[78] and Grim[71] found that soils containing kaolinite and montmorillonite can both develop from the same parent rock under different conditions of climate, topography and time. The same is also true in case of Indian soils, as Tiwary[34], while working on the black soils of Putida (Bihar), reported that shale parent material, having pyroxenes, hornblende, felspar, mica, etc., was the potential source for the development of montmorillonite and illite. He also pointed out that these minerals on further weathering decomposed into kaolinite under chemical environment of alteration, internal moisture and oxidation, conditioned by topography. According to Dhawan and Kahlon[29] the montmorillonite type of clay mineral was characteristic of an early mica of an intermediate, and kaolinite of an advanced stage of weathering. Ferromagnesium minerals (augite, hornblende and pyroxenes) had been reported to produce montmorillonite type of clays whereas felspar formed kaolinite. On the other hand, granites and pegmatites produced kaolinite; and mica, slate and shales formed illite type of clay minerals[79]. Shales and slates were also considered responsible for the development of illite and chlorite in saline and alkali soils of Punjab[62]. Felspar and muscovite in the primary mineral fraction were the chief agents for the formation of kaolinite and illite in the red soils of Ranchi and Netarhat[44], whereas the illite in Hazaribagh and Tatanagar soils was due to the occurrence of chlorite in the sand fraction in these soils. According to Das and Das[50], the brown and black soils of Karnataka developed under similar type of parent material such as blue granites, chloritic, hornblende, and micaceous schists and foliated metamorphic rocks had 2:1 type lattice minerals as the dominant fraction with small amounts of kaolinite and also in some cases degraded illite and vermiculite. The origin of kaolinite in laterite soils of western ghats was from granites, gneisses and schists, under high rainfall conditions[50]. Krishnaswami and Gupta[80], and Gupta[81] while working the mineralogical composition of soils and sands of Rajasthan, found the felspar mostly in the kaolinized form. Montmorillonite as the dominant clay mineral had been obtained by Krishnamurti and Satyanarayana[72] in desert soil of Western Rajasthan under high rainfall conditions. Illite and chlorite were the altered products of soil forming rocks (garnetiferrous biotite, granite, gneiss, schists and phyllites) of Kumaon Division, in central and western U. P., while montmorillonite in eastern region was originated from Bundelkhand gneiss, consisting of minerals, such as red orthodase felspar, a white plagioclastic felspar, quartz, hornblende, chlorite and mica[67]. The genesis of clay minerals in relation to parent material and environment was studied in three Indian soils of arid tropical zone by Datta and Adhikari[82–85] and observed that ferromagnesian silicates (biotite, chlorite, amphiboles, etc.) in fine sand were associated with magnesium-bearing secondary minerals in the clay when the intensity of weathering was low to moderate, with illite as the dominant part. But when both the alkali and alkaline earths constituted the parent rock, weathering of low to moderate intensity resulted in magnesium-bearing clay minerals such as chlorite, vermiculite and montmorillonite with small amount of illite.

Calcareous type of parent material, such as limestone, was favourable for the development of montmorillonite but it blocked the formation of kaolinite, whereas the potash rich parent material was responsible for the formation of illite[28]. It was also the finding of Gupta[16]. Acidic igenous rocks favoured the genesis of illite[6], whereas montmorillonite was the altered product of basic igneous and sedimentary rocks[33]. Basalt type of parent material, low rainfall and temperature, impeded drainage and scanty plant cover were the more important agencies responsible for the genesis of montmorillonite in the black soils of Bijapur[86]. Tamhane and Karale[87] while studying four virgin clay soils, found that basalt weathered primarily to montmorillonite, which subsequently decomposed into kaolinite under high rainfall conditions. Biswas, Narayana and Vasudevarao[88], while studying the soils of catenary sequence of Kurnool district (Andhra Pradesh), and Gawande, Das and Biswas[89] of Madhya Pradesh, concluded that illite was the dominant mineral of the upper and middle slopes but the montmorillonite predominated at the base. The later scientists also observed the degraded type of illite in the upland soil, which was due to excessive leaching.

The high concentration of alkaline-earth cations in exchangeable form and high pH values of soils favoured the stability of montmorillonite[90,91]. Aridity of region coupled with saline environment was responsible for the production of illite in Delhi and Karnal soil clays. Recently, Das and Das[44] investigated that the development of montmorillonite in black and brown soils of Mysore was due to slow weathering of felspar in alkaline environment, while kaolinite resulted in from complete hydrolysis of felspar. They also pointed out that small amounts of chlorite and vermiculite in these soils was due to the chloritic crystalline schists. Similar results had already been obtained by Egawa and Watanabe[92]. In general, kaolinite was predominant in perhumid regions while in semi-arid and arid regions having particularly high alkaline-earth contents, montmorillonite was the dominant mineral with a small amount of montmorillonite under moderate leaching conditions[82–85].

Summary and Conclusions

The presence of different clay minerals in various groups of soils of India enumerated above may be summarized as follows:

Sl. No.	Great Soil Group	State of Occurrence	Dominant Clay Minerals
1.	Alluvial soils	Punjab, Uttar Pradesh, Bihar, West Bengal, Assam, Orissa, Madhya Pradesh, Parts of Rajasthan & Jammu & Kashmir	Illite, kaolinite
2.	Black Soils	Andhra Pradesh, Madhya Pradesh, Maharashtra, Gujarat & Parts of Karnataka, Tamil Nadu, Bihar & Uttar Pradesh	Montmorillonite, beidellite
3.	Red Soils	Karnataka, Tamil Nadu, South & East Maharastra, East of Andhra Pradesh, Madhya Pradesh, Chota Nagpur region of Bihar and Parts of W. Bengal & Uttar Pradesh	Kaolinite, illite

Sl. No.	Great Soils Group	State of Occurrence	Dominant Clay Minerals
4.	Laterite and lateritic soils	Summits of hills of Deccan, Madhya Pradesh, the Rajmahal hills, Eastern Ghat, Parts of Orissa, Assam, Karnataka, Malabar & Western Ghat	Kaolinite or kaolin-like minerals
5.	Mountain & Hill soils	Parts of Kashmir, Assam, Uttar Pradesh, West Bengal, Himachal Pradesh & Bihar	Illite, kaolinite
6.	Brown or grey brown podsolic soils	Himachal Pradesh, Parts of Uttar Pradesh & Jammu & Kashmir	Hydrous mica, illite
7.	Brown forest soils	Uttar Pradesh, Himachal Pradesh, Jammu & Kashmir,	Illite, kaolinite
8.	Desert soils	Rajasthan, South Punjab, Haryana	Illite, chlorite, attapulgite
9.	Saline and alkali	Bihar, Punjab, Uttar-Pradesh, Haryana, Rajasthan & Jammu & Kashmir	Illite, kaolinite, chlorite
10.	Marshy and Peaty soils	Kerala, Coastal tracts of Orissa, North Bihar	Montmorillonite

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[Original mss. received on May 16, 1973]

UDC 668.3 : 678.7 : 66–977

A quick-setting adhesive based on epoxy resin and hardener suitable for use at 80°C was developed in this laboratory and used in the electrolyser plant at FCI Ltd., Nangal to check the gas leakages from the corroded frames, panels, nozzles, etc. The physical and chemical properties of the cured product (adhesive) were found better than those of the product used earlier in the same plant.

A Quick-Setting Adhesive from Epoxy Resin for Use at High Temperature

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The Nangal unit of FCI Ltd. for its Electrolyser Plant was in need of an adhesive to check gas leakages from the corroded frames, panels and nozzles, etc., which occurred often and had to be stopped immediately. The temperature at the joining points was around 70-80°C.

Based on the previous studies[1-3], a suitable hardener for epoxy resin and subsequently a formulation were developed to meet the specific conditions of the plant. Earlier, an adhesive having the trade mark Griptite was used.

This note reports the development of a suitable adhesive and its physical and chemical properties. A comparison of various properties has also been made with the adhesive used earlier in the plant. The demand is about 600 kg. annually.

Experimental

Amidopolyamine, a curing agent for epoxy resin developed earlier[1,2], when mixed with liquid epoxy resin, sets to a hard mass within 24 hr. The hardener can be modified by incorporating various types of additives, viz. acids, amines, anhydrides, etc. in different quantities, either alone or in combination, to decrease the pot life. Such a successful hardener was developed to give a pot life of 5-10 min. at 80°C when mixed with epoxy resin. The hardener, thus developed, was amber in colour and free-flowing, having an amine value 290-310, viscosity 14-16 poise at 30°C. and density 0.96 g./cc.

Properties of the Cured Product

Epoxy resin, having epoxy equivalent 180-200, was used and mixed with the hardener and was allowed to cure at 80°C. for 1 hr. Its physical properties, such as adhesive and shear strengths and Vicat softening point, were determined (Table 1). Its chemical properties are given in Table 2.

For comparison, the properties of the hardener and resin and their cured product used previously in the

TABLE 1—PHYSICAL PROPERTIES OF THE CURED PRODUCT

Physical Properties	Cured Product Using Hardener Developed in this Laboratory	Cured Product Used Previously at Nangal
Adhesive Strength, psi	430	430
Shear Strength, psi	900	775
Vicat Softening Point,*°C	78°	†

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*Vicat Softening Point under 5 Kp (4.45 kg) load.

†Sample could not stand 5 Kp load even at room temperature.

TABLE 2—CHEMICAL PROPERTIES OF THE CURED PRODUCT

Chemical	Cured Product Using	Weight Increase, %						
		1st day	2nd day	3rd day	4th day	5th day	6th day	7th day
20% Sodium hydroxide	Resin and hardener**	0.1627	0.2611	0.3535	0.4294	0.4581	0.4966	0.5272
	Resin & Hardener Previously Used at Nangal	1.269	1.652	2.012	2.273	2.485	2.691	2.877
Distilled Water	Resin & Hardener**	0.4141	0.5788	0.7031	0.7847	0.8608	0.9198	0.9632
	Resin & Hardener Previously Used at Nangal	8.389	10.71	12.85	14.45	15.77	17.01	18.35

**Hardener developed in this laboratory.

same plant were also determined. The epoyx equivalent of the resin was 200 and hardener of 650 amine value was found.

Conclusion

From Tables 1 and 2, it is evident that, in general, the properties of the cured product developed in this laboratory are better than those of the adhesive used earlier at Nangal.

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[Original mss. received on July 19, 1973]

UDC 543.852: 546.47+546.72

An approach has been made to estimate quantitatively the amount of acidity of a solution containing hydrolyzable ions of zinc and iron. Hydrolysis of these ions is suitably suppressed by complexation followed by precipitation with potassium ferrocyanide, thus allowing the quantitative estimation of the free acid by indicator, conductometric and potentiometric methods.

Determination of Free Acidity of a Solution in Presence of Zinc and Iron Ions

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Determination of free acidity of the reaction mixture is important in the production of zinc sulphate from metallic zinc and sulphuric acid. This acidity as the reaction proceeds gives the measure of completion of the reaction. So far there is no standard procedure for measuring the acidity of the reaction mixture.

Free acidity determination by direct pH measurement of the solution is not possible as the solution is highly acidic, viz. greater than 1 M., and in the determination of pH within the range 0—1, an error of ± 0.1+0.3 pH is introduced; in addition error may also get introduced because of high ionic strength of the solution[1].

On the other hand, the determination of acidity by titration with an alakli using phenolphthalein as the indicator or by conductometric or by potentiometric methods were found not suitable because of the hydrolyzable nature of zinc and iron ions. Thus, when experiments were conducted with an artificial mixture of zinc sulphate, ferrous sulphate and water containing varying amount of acids, having more or less the same composition as that of the reaction mixture obtained by treating zinc dross* with 20 per cent sulphuric acid, high values were obtained for the free acid [Table 1 (A, B & C)].

The determination of acidity appeared to have been influenced by the presence of hydrolysable ions, like Zn^{2+}, Fe^{2+} and Fe^{3+}, in the experimental solution.

The actual mechanism of hydrolysis of ions, like zinc or iron ions, does not seem to follow straightforward course. It proceeds through the formation of $FeOH^{2+}$ for ferric ions and $Zn(OH)^{+}$ for zinc ions, giving other products as composition of the reaction mixture varies. Acid complexes[2,3], such as $Fe(OH)(HSO_4)_2$ and $ZnSO_4$ $4\,Zn(OH)_2\,x\,H_2O$, for respective ions are also present.

TABLE 1—Estimation of Acidity by Alkali Using Indicator, Conductometric and Potentiometric Titrations

Amount of Acid Added, mol/lit.	Amount of Acid Estimated, mol/lit.	Difference, mol/lit.
A—By Alkali Titration Using Phenolphthalein as Indicator		
5×10^{-3}	7.3×10^{-3}	2.0×10^{-3}
5×10^{-4}	7.5×10^{-4}	2.5×10^{-4}
5×10^{-5}	7.8×10^{-5}	2.8×10^{-5}
B—By Conductometric Titration		
5×10^{-3}	5.45×10^{-3}	0.45×10^{-3}
5×10^{-4}	5.40×10^{-4}	0.40×10^{-4}
5×10^{-5}	5.42×10^{-5}	0.42×10^{-5}
C—By Potentiometric Titration		
5×10^{-3}	5.56×10^{-3}	0.56×10^{-3}
5×10^{-4}	5.59×10^{-4}	0.59×10^{-4}
5×10^{-5}	5.63×10^{-5}	0.63×10^{-5}

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*containing zinc 94.5, iron 4.5, aluminium 1 and lead 0.45 per cent.

The hydrolysis of zinc sulphate proceeds according to the following equations[4] :

$$ZnSO_4 + H_2O \rightarrow Zn\,(OH)^+ + H^+ \qquad (1)$$

The released hydrogen ions may be partially responsible for the higher result obtained by the three methods of titration and hence for the shifting of curves towards the higher side in the cases of conductometric and potentiometric methods (Figs. 1 and 2).

However, if the hydrolysis of the ions is suitably suppressed by complexation or precipitation following complexation, the free acid could be determined with sufficient accuracy. In this study potassium ferrocyanide has been used for suppressing the hydrolysis of zinc and iron ions by complex formation and then precipitating them[5,6] as $Zn_2\,Fe\,(CN)_6$ and $K_2\,Fe\,[Fe(CN)_6]$.

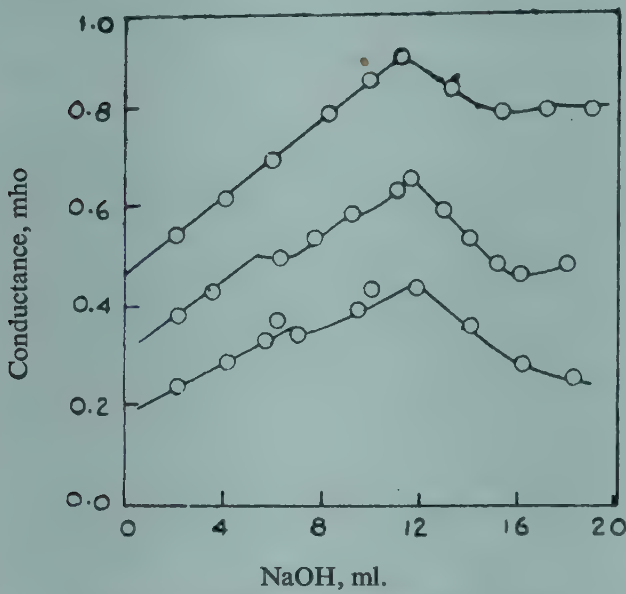

Fig. 1—Variation of Conductance of the Solution with Added Alkali

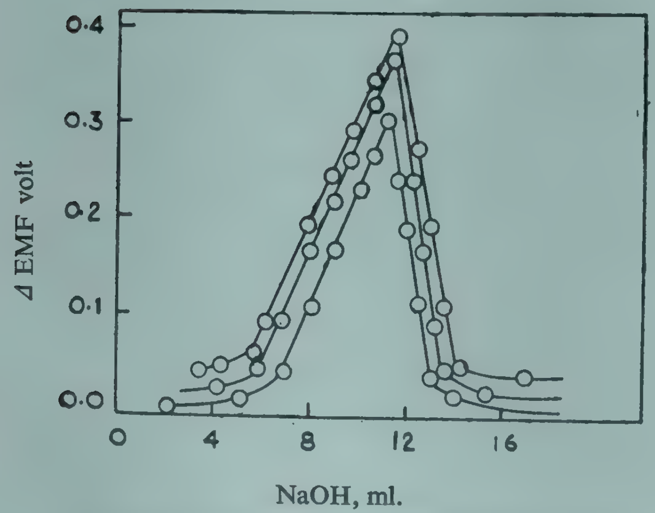

Fig. 2—Plot of Change of EMF with Added Alkali

Experimental

An artificial solution was prepared by dissolving 20 g. zinc sulphate and 1.5 g iron sulphate in 80 ml distilled water. 10 ml of this stock solution was taken in a pyrex glass container, in which a known amount of sulphuric acid and an excess amount of potassium ferrocyanide solution (20 per cent) were added. All chemicals used were of BDH Analar quality. All titrations were made using a known strength of sodium hydroxide solution. Conductometric titrations were made using Philips conductance bridge while potentiometric titrations were carried out using a Cambridge pH meter having a glass electrode and saturated calomel as the reference electrode, and the connection was made through an agar/agar bridge.

Results and Discussion

The determination of known amounts of acid in the presence of zinc and iron ions by the three methods are given in Table 2 (A, B & C). In each case the difference between the acid added (known) and acid found after titration bears a good agreement, but the best agreement is achieved by the potentiometric method.

The general course of acid-base titration in presence of potassium ferrocyanide as complexing agent was interesting. Before the addition of the complexing agent, the solution was colourless but it changed immediately to either light yellow or blue colour depending upon the

TABLE 2—ESTIMATION OF ACIDITY BY ALKALI USING INDICATOR, CONDUCTOMETRIC AND POTENTIOMETRIC TITRATIONS USING A COMPLEXING AGENT

Amount of Acid Added, mole/lit.	Amount of Acid Estimated, mole/lit.	Difference, mole/lit.
	A—*By Alkali Titration Using Phenolphalein as Indicator*	
5×10^{-3}	5.0×10^{3}	0.0
5×10^{-4}	5.1×10^{4}	0.1×10^{-4}
5×10^{-5}	5.06×10^{-5}	0.06×10^{-5}
	B—*By Conductometric Titration*	
5×10^{-3}	5.01×10^{-3}	0.01×10^{-3}
5×10^{-4}	5.002×10^{-4}	0.002×10^{-4}
5×10^{-5}	5.10×10^{-5}	0.01×10^{-5}
	C—*By Potentiometric Titration*	
5×10^{-3}	5.001×10^{-3}	0.001×10^{-3}
5×10^{-4}	5.008×10^{-4}	0.008×10^{-4}
5×10^{-5}	5.001×10^{-5}	0.001×10^{-5}

amount of acid added after mixing with potassium ferrocyanide. When the acid concentration in this solution was high, the colour of the reaction mixture after the addition of potassium ferrocyanide was light yellow which gradually turned blue and then intense blue with further addition of alkali. But finally at the nearing of the end point, there was an abrupt disappearance of blue colour. When the amount of acid added was of the order of 10^{-3} g. mole/lit. a faint blue colour was observed with the addition of potassium ferrocyanide which depend on the addition of alkali. Here also the disappearence of colour was noticed just before the end-point. When the amount of acid added was as low as 10^{-5} g. mole/lit., the initial colour of the mixture was deep blue when the complexing agent was added which persisted throughout the course of addition of alkali till the end point was reached when it vanished.

The course of the chemical reaction may be followed as equations (2) and (3).

$$2\,ZnSO_4 + K_4[Fe\,(CN)_6] = Zn_2[Fe\,(CN)_6] + 2K_2SO_4 \quad (2)$$
$$Fe\,SO_4 + K_4[Fe\,(CN)_6] = K_2Fe\,[Fe(CN)_6] + K_2SO_4 \quad (3)$$

As the experiments were conducted in the atmosphere there was every chance of aerial oxidation of ferrous to ferric sulphate which reacts with the complexing agent giving the prussian blue coloured complex as follows:

$$2\,Fe_2(SO_4)_3 + 3\,K_4\,[Fe(CN)_6] = Fe_4\,[Fe(CN)_6]_3 + 6K_2SO_4 \quad (4)$$

When the acid concentration was high partial dissociation of potassium ferrocyanide was possible according to equation (5)

$$K_4\,[Fe(CN)_6] + 3H_2SO_4 = 6HCN + FeSO_4 + 2\,K_2SO_4 \quad (5)$$

The liberation of hydrocyanic acid could inhibit the oxidation of ferrous to ferric sulphate thereby developing a blue colour. With reduced acid concentration, the dissociation of potassium ferrocyanide was inhibited and aerial oxidation of iron salt was made possible. That is why blue colour was noticed when the acid concentration was in the order of 10^{-5} g.mole./lit.

Further, as the acid was getting neutralized with alkali, aerial oxidation progressed producing more intense blue colour. As the end-point was reached, the ferric complex appeared to get decomposed resulting in the disappearance of the blue colour, which was confirmed by a separate experiment. At this stage, one or two drops of alkali completed the titration with the appearance of the pink colour of the indicator, phenolphthalein.

It is found (Fig. 3) that the conductance breaks are quite regular yelding the exact amount of acid in the solution. The plot 3A (Fig. 3) for the solution containing

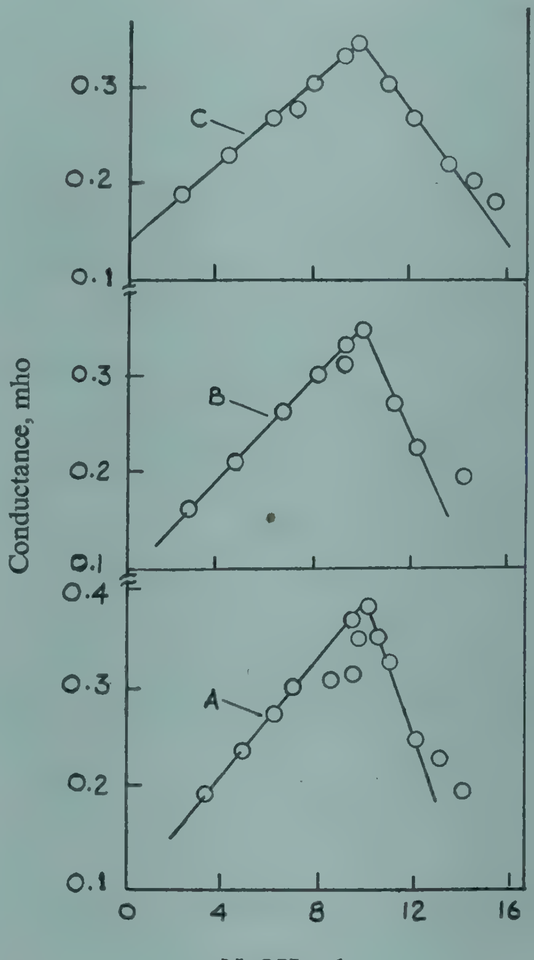

Fig. 3—Variation of Conductance of the Solution Containing Complexant with Added Alkali

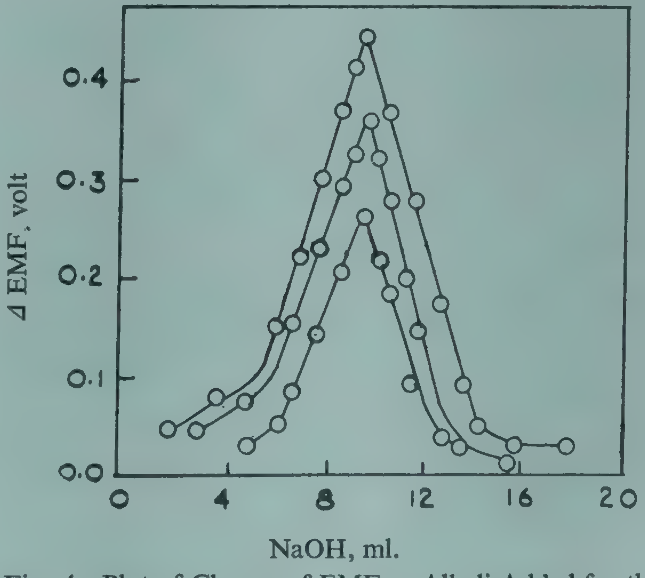

Fig. 4—Plot of Change of EMF vs Alkali Added for the Solution Containing Complexant.

high concentration of acid gave one more break before the neutral point. This type of break is seen only in case of 10^{-2} g. mol/lit acid range. Therefore, the break may correspond to the neutralization of reducing agent HCN, favouring the formation of the coloured complex $Fe_4\,[Fe\,Fe(CN)_6]_3$ [eqn. (4)]

The potentiometric method 3 seems to be the best of the three; the coloration developed in the reaction mixture did not impose any limitation. On the other hand, e. m. f. values are not affected by extra ion formation and its consumption. The plots of E vs V gives uniformly nice peaks (Fig. 4) which are accurate measures of the amount of acid present. Regarding the liberation of hydrocyanic acid and its consumption during titration, the potentiometric e. m. f. does not get affected as it is equivalent to the amount of sulphuric acid consumed and secondly, the pK_a values of these two acids are closely approaching.

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[Original mss. received on April 3, 1973]

UDC 546.28: 541.182.5: 541.6

The pores of a silica gel were modified by treatment with aqueous solutions of mineral acids and some salts. The resulting changes in the micropore structure have been analysed by using the MP-method of Brunauer.

Modification of Micropore Structure in Chemically-Treated Silica Gels

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Introduction

Silica gels have wide applications, viz. as supports for industrial catalysts, as desiccants and also as adsorbents in gas chromatography. They generally possess very high surface area having pore patterns often extending to micropore region. The size distribution, shape and orientation of pores in these gels are important parameters for controlling the rates of reactant transport in packed bed reactors. The preparation conditions and subsequent physico-chemical treatments can control the surface and pore characteristics of the gels. But sometimes it is required to change the existing pore structure of a finished gel to suit specific applications.

Thermal sintering is a convenient method which is frequently used to obtain wide pore gels from those having predominantly micropore distribution. Another popular method is to coat the gel pores with organic or inorganic chemicals[1–5] to obtain gels of the desired pore structure. Okkerse and DeBoer[3] and Naidu *et al*[6] have reported the changes in micropore structure when the finished gels are subjected to treatment with aqueous solutions of mineral acids and salts.

The present note gives the results of micropore structure modification of the gels when treated with aqueous solutions of mineral acids and some salts.

Experimental

The samples were prepared by the method reported earlier[6]. The low temperature nitrogen isotherms were obtained by the Adsorptomat.* The other physico-chemical data, such as total pore volume and average pore and particle sizes, were determined by the usual methods.

Results and Discussion

The MP method of Brunauer[7] was used for the micropore analysis of the original and treated gels. The complete pore structure of the original gels is given in Table 1.

TABLE 1—Pore Data for the Untreated Gel

Pore Group	Si, m²/g.	(S_i-S_{i+i}), m²/g.	Mean r_h, Å	V_i, ml/g. From slope	V_i, ml/g. From intercept
1.	357	179	4.25	0.076	0.076
2.	280	77	5.50	0.042	0.044
3.	193	87	6.50	0.056	0.056
4.	113	80	7.50	0.061	0.061
5.	81	32	8.50	0.027	0.027
6.	52	29	9.50	0.027	0.026
7.	29	7	10.50	0.024	0.024
8.	16	13	11.50	0.015	0.016
9.	4	12	13.50	0.015	0.014
10.	—	—	15.00	—	0.006

S_{BET}=560.0 m²/g.; S_t=536 m²/g.; T.P.V.=0.36 cc./g.

The analysis is based on the t-values of De Boer for the adsorbed nitrogen film thickness. Brunauer[7] obtained the pore volumes (V_i) of the different groups of pores by using the following equation:

$$V_i = 10^{-4} (S_1 - S_2). \frac{t_1+t_2}{2}$$

where S_1 and S_2 are the surface areas obtained from the slopes 1 and 2 of the V_i-t curves, and t_1 and t_2 are the thicknesses of the films in the narrowest and the widest pores of the group (Fig.1). In the present calculations, however, these values were obtained by directly substracting the intercept at the ordinate made by tangents drawn at suitable intervals. The V_i values obtained by both the procedures agree very well (Table 1). The calculations for all other samples were, therefore, made by the direct subtraction method only.

It can be seen that the V_i-t plot of the original gel (Fig. 1) leans towards the x-axis indicating that the sample must predominantly contain micropores[8]. The derivative curve (Fig. 2) of the pore size distribution for

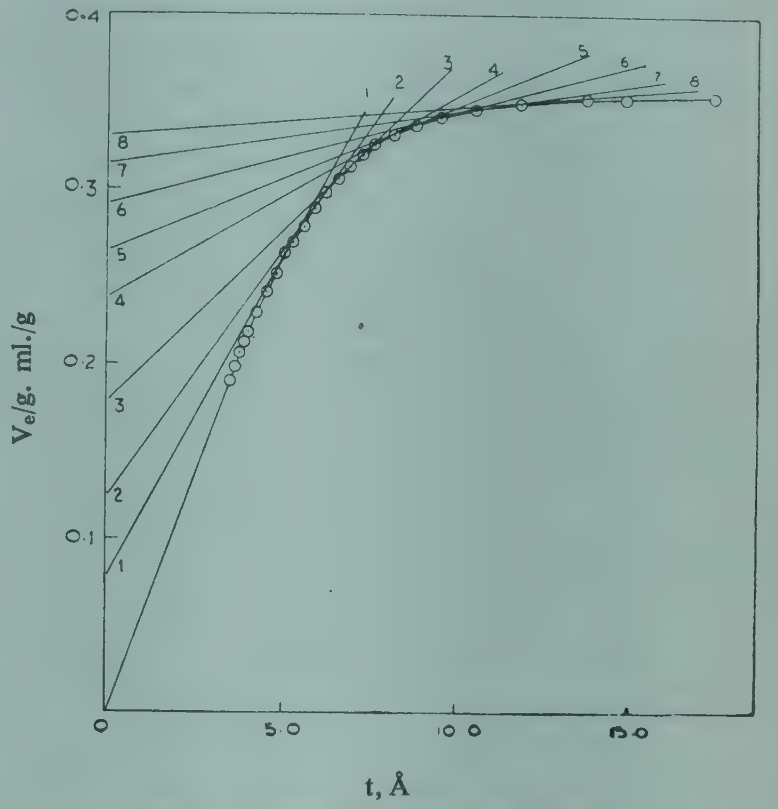

Fig. 1—Adsorption-desorption Isotherm Converted into a De Boer V_e-t Plot

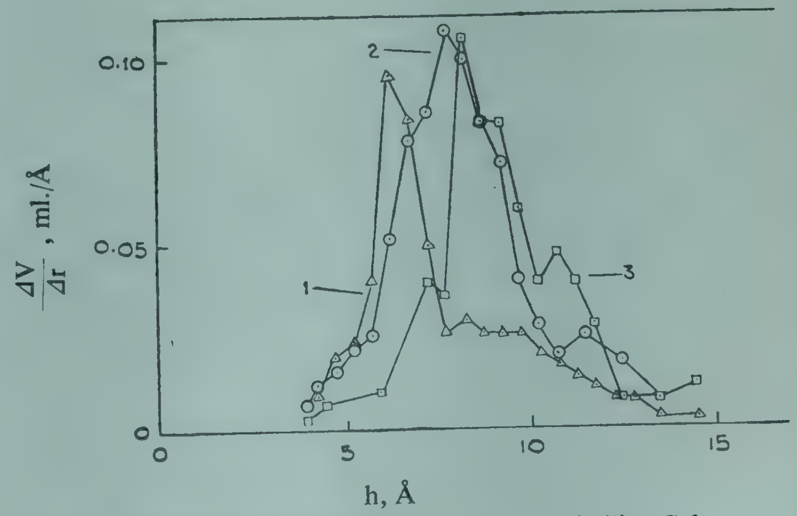

Fig. 2—Pore Volume Distribution Curves of Silica Gel.
1. Original
2. IM HCl
3. Distilled Water

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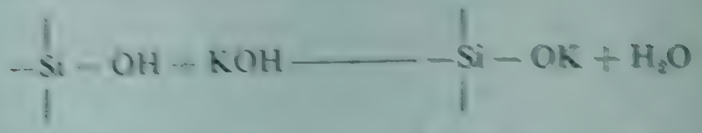
*instrument for obtaining nitrogen adsorption isotherm, manufactured by American Instrument Co., USA.

this gel shows that more than half of the total pore volume is present within a hydraulic radius (r_h) range of 5-7 Å. The rest is distributed over comparatively wider range of $r_h=7$ to 14 Å. The only maximum in the curve occurs at $r_h=6.2$ Å, i. e. if the pores are cylindrical in shape, those of 12.4 Å predominate. The calculated average pore radius for the original gel is $\bar{r}_p=12.8$ Å ($\bar{r}_p=2\,V/S$, where V is the total pore volume and S is the BET surface area).

The maximum of the p. s. d. curve for the water treated gel (Fig. 2) shifted from $r_{cp}=12.4$ Å to $r_{cp}=16.4$ Å with concomitant slight broadening of the peak, where r_{cp} is the radius of the pore assuming a cylindrical model. The average pore radius of the gel increased from 12.8 to 18.1 Å. Okkerse and DeBoer[8] in their studies on amorphous silica have shown that pure distilled water drastically decreased the surface area of the gel and concluded that the mechanism of pore modification may be one of dissolutions of the silica from the surface of wider pore region and an interaction of this dissolved silica with the hydroxyl groups of the smaller pore regions, thus facilitating the growth of elementary particles and increasing the pore radius. In the present case also, a drastic reduction in surface area by more than 21 per cent was observed after water treatment. The phenomenon may be considered analogous to an aqueous sintering process in which small pores get blocked by the silica removed from the large pores, thereby creating more of the wider pores resulting in the formation of larger grains.

The distribution of the micropores is also shown for the gel treated with 1.0 M hydrochloric acid. On comparison with the original gel, it is observed that the pore volume has increased from 0.36 to 0.45 ml./g. and the surface area decreased to 539 m²/g. The pores of the treated gel are distributed over wider pore region compared to the original gel. Treating the gel with stronger acids, viz. 7.0 and 10.0 M, increased the average pore size to 28 and 33.4 Å respectively. Further increase in the concentration to 14.0 M has, however, made no change in the pore structure. With sulphuric acid, as the concentration of the acid was increased from 14.0 to 47.0 M, the effect of the pore modification reduced so much that at 47.0 M, the average pore radius is 13.7 Å and is comparable to the average pore radius of the original gel which is 12.8 Å.

The liquid phase adsorption of metal ions, such as K+ or Na+, on silica gels is a well-known phenomenon[9]. The adsorption of cations is generally attributed to the presence of hydroxyl groups, which are formed as residues from the poly-condensation of the silicic acid, localized on the surface of the silica gels. The mode of cation adsorption may be as given below:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH}+\mathrm{KOH}\longrightarrow-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OK}+\mathrm{H_2O}$$

According to Imelik,[10] the extent of adsorption of cations on silica gel depends on the nature of the electrolyte. Thus, hydroxides are expected to be much more easily adsorbed than the salts, where the adsorption of anions occurs simultaneously with the cations. An attempt was made in the present case to determine qualitatively the adosorbed cations in gel, by leaching the salt-treated gels with hydrochloric acid on a water bath. The extracts were examined by a flame photometer which showed none of the Na^+, K^+ or Ca^{2+} ions with which the gel was treated. This may be due to the negligible adsorption of the ions as these were derived from their corresponding halides and nitrates for the treatment. Imelik[10] suggested that during the process of drying, even at moderate temperatures, the cations adsorbed on surface hydroxyl groups may enter into the silica gel lattice, giving rise to a structure similar to that of an alkali silicate glass. Such a possibility will also make it difficult to leach out the cations by digesting with hydrochloric acid.

In Fig. 3 the pore size distribution of the gel treated with inorganic salts has been shown. The treated gels have been found to retain micropores though with a slight change in the distribution. The treatment with 4.0 M potassium chloride followed by desorption of water at 110°C decreased the surface area slightly. The hysteresis loop of the nitrogen isotherm (not shown) shifted towards higher relative pressures and the desorption branch became steeper compared to the one for the original gel.

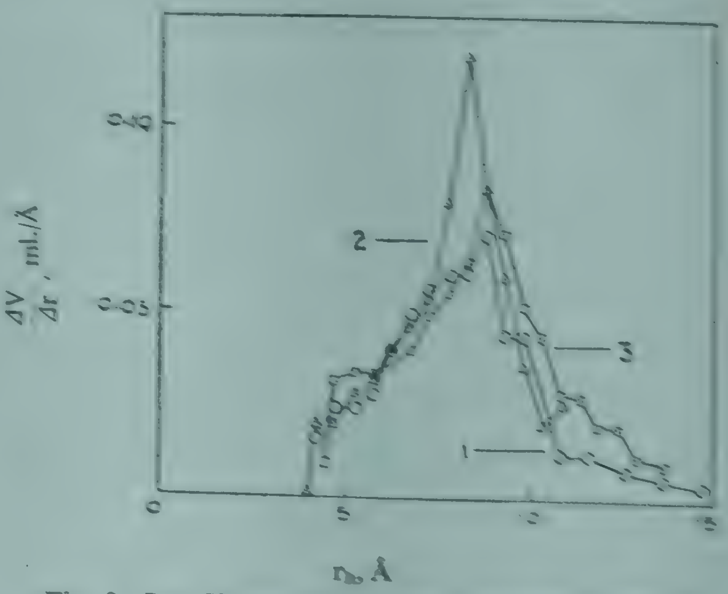
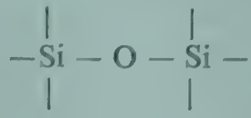


Fig. 3—Pore Volume Distribution Curves of Silica Gel.

The analysis of the micropore structure provides further necessary details and enables one to follow in a precise manner the modifications brought about in the texture of the gel. The distribution of the small pores spreads over wider pore radii after the salt treatment. The proportion of the pores between the $r_h=5.5$ Å and $r_h=7.5$ Å is only 30 per cent, while it was not less than 50 per cent in the original gel within the same range. The maximum in the pore size distribution shifted from $r_h=6.2$ Å in the original to $r_h=8.3$ Å in the treated gel, thus increasing the population of bigger pores.

The adsorption of calcium and sodium ions on silica gel gave rise to modifications somewhat different from those obtained for the potassium ion. The sintering in terms of pore radius has been found a bit more marked in this case. Contrary to the results with potassium, sodium and calcium caused the pore distribution to become broader. A new peak appeared at $r_h=8.5$ Å for both sodium and calcium treated gels. The average pore radius $\bar{r}_p=2\ V/S$ for calcium treated gel is 14.1 Å which is less than the corresponding value 17.0 Å for sodium treatment because the total pore volume in the case of the former is confined in the pores of lower pore radius. Analysis of the hysteresis loop of nitrogen isotherm at −195°C also confirmed this conclusion. The smaller pores ($r_h=7.5$ Å) have undergone an almost similar change with all the three electrolytes. These changes in the surface properties can be explained if one assumes that the adsorbed cations, as a result of the drying operations enter into the lattice of the silica causing the rupture of a certain number of



$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-$bridges[10].

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[Original mss. received on Oct. 16, 1973]

Technical Digest

Non Destructive Testing

The science of nondestructive testing (NDT) is widely used all over the world in such sophisticated industries, like space and nuclear technology, aircraft and automobile industries, defence equipment production, heavy industries like steel, chemicals and fertilizers, etc. The well advanced techniques of NDT are used in foreign countries to avoid industrial failures. But in India this science is still in its infancy. The role of nondestructive testing in preventing premature failures is now widely appreciated because premature failures in any industry lead to accidents which result in heavy production loss, sometimes loss of human lives and in many cases damage to costly equipments, especially inported ones. All this has necessitated devising ways and means to control accidents and minimize failures and non-destructive testing is a handy and reliable tool. An advantage in NDT is that the material under examination does not undergo any physical change or dimensional distortion.

The ever increasing importance of NDT in all industries especially in fertilizer industry has led P & D Division of FCI Ltd. to establish a full-fledged non-destructive testing laboratory which is now well-equipped with modern equipments. It renders services right from the beginning of setting-up of fertilizer plant. The scope of services include (1) inspection of materials of construction and fabrication, (2) inspection of finished equipments at shop floor, (3) testing of weldments in high pressure/temperature lines of critical equipment like horton-sphere, flue gas boiler, etc. which are fabricated at site, (4) inspection during commissioning and (5) systematic periodic inspection in running plants as a preventive measure.

Some of the routine methods employed are: (1) liquid penetrant testing: used on metal, glass, ceramics to locate surface discontinuities; (2) magnetic particle testing: used on ferromagnetic materials to detect surface or subsurface discontinuities; (3) radiographic testing (x-rays and gamma-rays): used for the inspection of the internals of pipe lines and equipment for corrosion and weld inspection; (4) eddy current testing: for surface and subsurface discontinuities, hardness, thickness, plating, coating; (5) ultrasonic testing used on any material. Based on the experience gained three papers which covered some of the research-oriented topics carried out by the scientists of NDT group were submitted to the Diamond Jubilee Convention of National Test House on 30th Oct. and 1 Nov. 1972 at Calcutta.

M/s G. S. Sinha and K. C. Banerji while carrying out extensive radiography of welded joints of thicker sections by x-rays observed a faint but consistent white line on some of the radiographs taken on a vessel fabricated out of 316L stainless steel, 12 mm. thick. The appearance of such phenomena, at times referred to as 'mottling', is quite frequent during inspection of thick castings or large single crystals. However, their appearance on stainless steel fabricated components, though rare, may be quite taxing to inspect or/and often mislead those entrusted with inspection of quality welds. The interpretation of this phenomena formed the theme of their paper 'White Line Problem in Radiography'. The experiments with tilted specimens confirmed that the appearance of the white line was due to an interference phenomenon, occurring out of the scattered x-ray radiations due to particular geometrical relationships between the grain size and wave length. It was a case of special form of scattering which is occasionally observed during radiography of metallic specimens whose grain size is comparable to specimen thickness, when a preferred parallelism is accidentally obtained in the directional orientation of the grains with respect to the incident beam. When a small source of radiation is placed close to a coarse grained poly-crystalline material, a symmetrical diffraction pattern of conics (white on radiograph) and reflection conics (black on radiograph) are sometimes produced in accordance with the Bragg relationship.

Nondestructive testing of heat exchanger tubes by eddy current methods provide a fast, reliable and comprehensive method. This method has the advantage of giving not only the surface defects such as thinning, cracks or corrosion pitting but also indicate the gross metallurgical sub-surface defects, such as inclusion, segregation, abrupt variation in heat treatment and internal voids, etc. At times it may be possible to locate defects entirely outside the tube, e.g. on the external surroundings of a tube by inspection from within and

Probolog Equipment_in Use

vice-versa. Enlargements of the openings in the baffle plates or resultant damage on the tubes at the baffles due to vibrations can also thus be examined without opening the shell side. Probolog inspection was carried out on about 12,000 new tubes used in the fabrication of the heat exchangers in order to make sure that the tubes which had passed during hydraulic tests did not contain any such defect. The technique of evaluation followed, particularly formulation of significance criteria for rejection of some S. S. 316L tubes imported by FCI Ltd., for heat exchanger fabrication for urea plants was described by M/s K. C. Banerji, Narayancharyula & Sri N. L. L. Murthy in a paper, 'Inspection of Heat Exchangers by Probolog'.

In heavy chemical industry suitably planned and executed thickness surveys help to estimate corrosion/erosion and reduce unexpected failures and idle hours due to shut down to minimum. M/s K. V. Sundaram and D. K. Thakur have outlined a procedure for the same in their paper, entitled 'Assessment of Corrosion/Erosion in Fertilizer Plants by Thickness Surveys'. They have pointed out that in practice this is done in two phases, viz. normal phase, i. e. when plant is in running condition, and shut-down phase, i. e. when plant is not in running condition and parts inaccessible. The large volume of collected data when analysed and plotted on the drawings give overall picture of condition of plant. In case of pipelines authors have suggested colour code. Some of the other suggestions made by the authors are: In vertical columnar equipment like the scrubbers two rows of points along the vertical, spaced at suitable intervals and a few points at the top and bottom ends, should prove sufficient. However, the efficiency and speed of measurement depend to a large extent on the easy approach to these points of measurement. This may be ensured by choosing the points in the vicinity of ladders and landings already available. In horizontally laid equipment, like storage tanks, heat exchangers, the shell thickness could be assessed by taking two rows of points one on the top and the other at the bottom. Thinning due to vapour will be more on top and that due to condensates more at the bottom. As thinning due to erosion is maximum at the bends it is advisable to cover all the bends. A reasonable number of spots have to be marked on the straight portions as well for the purposes of comparison. In low pressure lines, equidistant markings at suitable intervals will be representative of the entire length. Pipe sections associated with similar equipment, like compressors and reactors, are similar. In these cases, continuous numbering may lead to difficulties of point identification. Using same marking numbers for similar locations on each section or stream, with different prefixes to denote the sections associated with the units may improve clarity of marking. In high pressure lines associated with compressors a four digit code was found to be convenient.

Then authors have cited the example of ammonia and urea plants in which they were able to detect the corrosion in time and quick remedial measures taken saved the further loss. Then they informed that some fertilizer factories have already taken up annual thickness surveys in their high pressure lines and further added that the ultrasonic pulse echo units, radiographic cameras, corrometer, probolog, battery operated miniature flaw detectors are some of the equipments used in these testings.

Notes & News

Kellog's Coal Gasification Process

Gasification of coal in a bath of molten sodium carbonate through which steam is passed is the basis of the Kellog coal gasification process. The bath molten salt offers several important advantages. First, sodium carbonate strongly catalyzes the basic steam-coal reaction permitting essentially complete gasification of coal at reduced temperature. Second, the molten salt can be used to supply heat to the coal undergoing gasification. Third, the molten bath serves to disperse coal and steam throughout the reactor, which permits direct gasification of caking coals and eliminates the need for carbonization of such coals. Fourth, the bath of salt operates at a uniform temperature in the gasification range and, continued with the catalytic effect of sodium carbonate on steam-carbon gasification, yields a raw gas that is free of tars as well as tar acids and bases.

Continued development of this process has led to a steady evolution of the design concepts applied to the system for coal gasification. The first process design made use of a circulating stream of molten salt between separate gasification and combustion, or heating zones. Gasification of coal in a single-vessel and convention to pipeline gas requires substantial additional processing in addition to the gasification operation which include coal preparation, oxygen generation, shift conversion, gas purification and methanation. To measure the economics of the gasification the basis chosen is a plant with an output of 250 billion Btu/day, the gas having a higher heating value of 947 Btu/std.cu. ft. Sufficient equipment design work was done to obtain dependable cost estimates for erection of the proposed plant, but some items, such as the coal and carbonate feed systems, may be improved with further detailed design work.

The estimated cost for an erected, completely integrated facility of the selected capacity is $ 155.5 million, to which a working capital of $ 7.8 million should be added to make a total capital investment of $ 163.3 million. This investment is for a plant built at today's prices and does not include interest during construction or contingencies. The 20 year average gas selling prices produced in this plant is estimated to be 66.1 c million Btu (62.6 c/thousand std.cuft.). Table 1 presents the items that make up the estimated cost, together with the major assumptions that have been used. Coal is charged at $ 4/ton, which is equivalent to 14.3c/million Btu. For comparison, a recent article estimates that coal mined in the Appalachian region in a strip mine of appropriate size can be delivered to the mine mouth for $ 4/ton after paying reclamation costs. Operating labor is charged at $ 4.75/man-hour, and capital charges are put in at 13% of plant investment per year. This was done to reflect utility financing in which the debt-equity ratio is 65:35, and interest (5%) and return (7%) are applied to the remaining undepreciated investment over the life of the plant (20 years) as specified in the OCR-AGA cost accounting procedure. Also included are local taxes, insurance, and depreciation.

If the interest on outstanding debt is 9%, return on utility rate base is 12%, and with coal at $ 6/ton, the gas selling price would be 80c/million Btu.

[*Chemical Engng. Proc.*, **69** (3) (1973), 31]

TABLE 1—ESTIMATED GAS SELLING PRICE

Bases: 250 ×109	Btu/day Pipeline Gas
947	Btu/std.cu.ft. Higher Heating Value
90%	Stream Efficiency

Fixed-Capital Investment	$ 155,500,000
Working Capital	$ 7,800,000

Item	Gas Cost 106 btu
Bituminous Coal at $ 4/ton	18.6
Sodium Carbonate Make-up at 1.55c/1b	2.3
Catalysts & Chemicals	1.6
Sulfur Credit at $ 10/ton	−0.4
Power at 6 mils/kw-hr	5.1
Operating Labor @$ 4.75/man-hr	1.7
Maintenance at 3% of Fixed Investment/yr	5.4
Supplies @ 15% of Maintenance	0.8
Supervision @ 10% of Operating Labor	0.2
Payroll Overhead @ 10% Operating Labor & Supervision	0.2
General Overhead at 50% (Maintenance + Supplies + Operating Labor + Supervision)	4.0
Depreciation @ 5% of Investment/yr	9.5
Local Taxes & Insurance @ 3% of Investment/yr	5.7
Total Operating Expense	54.7
20 yr. Average Gas Selling Price ($ 4/ton coal)	66.1*
20 yr. Average Gas Selling Price ($ 6/ton coal)	80.0**

*65:35 debt-equity ratio, 5% interest on debt, 7% return on rate base
**65:35 debt-equity ratio, 9% interest on debt, 12% return on rate base
+Using OCR-AGA cost accounting procedure

Superphosphate Plant for Nigeria

Nigeria will have its first fertilizer plant in the Kaduna region. The plant, to produce 100,000 tons of superphosphate per year, will be built by three Japanese firms on a turn-key basis. Nissan process will be used for preparing the superphosphate.

Nissan Process: It is the most economical and easy process developed by Nissan Chemicals from over ninety years of experience. Among the various characteristics, the following need mention (1) Cost of construction and maintenance is low. All the materials used in this process are made of such materials that are suitable for effective erosion of single superphosphate and for cheimcal conditions of gas. Life of the equipment is long, and maintenance is easy. (2) Operation is flexible. The mixed, continuous den is designed in such a way so that varied grades of the fertilizers can be produced in the same device. Grades can also be changed quickly. (3) Thorough consideration is given to the prevention of public hazards such as dust and fluorine gas. Dusts are completely collected with cyclone scrubbers and big filters installed at various places. The combination of jet scrubber and turbulent contact absorber reduced the gas content from tens of thousands ppm at the den outlet to less than 50 ppm at the stack gate.

Reaction & Process: Phosphate ore of 200 mesh-pass 70 per cent and 100 mesh-pass 90 per cent is crushed. Mixed with circulatory air, it is allowed to enter the cyclone. The rock is gathered and sent to the ground rock hopper, while air is sent back to the mill with a circulation fan. The ground rock is made to react with sulphuric acid (98 per cent sulphuric acid is diluted to 70 per cent and cooled) in a paddle type mixer. The mixture is, then supplied to the continuous den. The single superphosphate, thus formed, is kept in the curing pile for 10 to 14 days until its solubility (AT/TP) rate rises to more than 99 per cent. The cured calcium superphosphate is formed into granule with a disc-type granulator. The granules are dried in the rotary dryer (here hot air of about 400°C is created in a heavy oil burning furnace) until moisture content fell to 2-4 per cent. Powder in the dryer and silicon tetrafluoride in the decomposition process is removed from the cyclone and sent to the waste gas disposing process. Dried granule are screened and the grade between 4.7 and 1.5 mm. are cooled in a vibrating cooler and placed in the bulk storage. The large granule are sent back to the crusher and recycled.

[*Look Japan*, **17** (1973), No. 205, p. 20]

Rapid Assay of Ammoniacal Nitrogen in Fertilizers

Ammoniacal or total nitrogen in the nitrogen-based fertilizers is determined commonly by the well known Kjeldahl procedure. This procedure involves the conversion of nitrogen into an ammonium salt and later distilling off ammonia and determining it by an alkalimetric procedure. But Kjeldahl procedure, apart from involving the risk of leakage, is a time-consuming operation. So an alternate procedure 'formal titrations' has been suggested for assaying of fertilizers.

This well known titrations procedure is speedier (3 titrations require 15-20 min.) and also does not involve any cumbersome distillation. In this method, ammonium salts react with formaldehyde and liberate an equivalent amount of acid, which is estimated by titration against a standard alkali.

$$4NH_4Cl + 6HCHO \rightarrow (CH_2)_6N_4 + 4HCl + 6H_2O$$

One equivalent of acid is liberated against each ammonium ion or an atom of nitrogen.

Determination of Ammonium Chloride and Ammonium Sulphate: Weigh 5g. of the material accurately and dissolve it in water. Make the volume to 500 ml. Add few drops of the methyl red indicator to an aliquot, usually 50 ml, and neutralize any free acid, if present, to methyl red end-point. To this, add 10 ml of 1:1 formaldehyde, neutralize to phenolphthalein end point and set aside the solution for 5 minutes. Titrate the acid generated by the formaldehyde reaction against standard alkali using phenolphthalein as the indicator.

Determination of Ammonium Phosphate: Formaldehyde, on addition to ammonium phosphate, liberate phosphoric acid.

$$2(NH_4)PO_4 + 6HCHO \rightarrow (CH_2)_6N_4 + 2H_3PO_4 + 6H_2O$$

Add 10 ml of formaldehyde (1:1) to an aliquot of ammonium phosphate and set aside the solution for 5 minutes. Add a pinch of sodium chloride and titrate the solution against standard alkali. The appearance of pinkish violet colour by adding a mixture of methyl red, methylene blue and phenolphthalein shows the end point.

Determination of Urea: Digest 5 g. of the material with 25 ml of sulphuric acid and 50 ml of water for 30-45 min. (till the solution is colourless). During this reaction, urea gets converted into ammonium sulphate. Cool the solution and dilute it to make a definite volume of 500 ml.

Add 10 ml of 1:1 formaldehyde to this and estimate ammonia as usual by the formal titration procedure. Methyl blue may be used as a screening agent to obtain the sharp and better end point.

The results which have been obtained with various samples in terms of percentage of nitrogen both by formal titration and Kjeldahl distillation method are quite comparable.

[*ISI, Bull.*, **25** (1973), 201]

OSW Design for Ammonia Converter Using Indirect Cooling

Oesterreichische Stickstoffwerke AG (OSW) of Linz (Austria) has designed a large sized converter for single-train ammonia plants, which employ the use of indirect heat-exchange for controlling the temperature within the large converter. No horizontal OSW converter has been built as yet but six vertical type converters have been constructed and are in use. The first OSW converter was started in 1965 at Eire with a 120 tpd capacity. The largest converter of this type for the 880 tpd plant, constructed by Uhde, was put into service in 1970 at Castrop-Rauxel, West Germany.

The cooling system, which is widely adopted in the designs of large converters (over 600 tpd), comprises more than one catalyst bed with intermediate cooling facilities between them. In one system, which employs quench cooling, cold synthesis gas is directly mixed with the hot reacting gases, either as they pass through the catalyst bed or, in a multiple bed converter, as they pass from one catalyst bed to the next. However, the horizontally mounted arrangement in Kellogg's converter has a number of other advantages. The internal cartridge containing all the catalyst beds can be rolled out from the pressure shell as a single unit instead of requiring heavy and powerful hoisting gear or separate drainage of the catalyst. Also the gas flow through the catalyst beds is transverse rather than axial. This arrangement makes possible the greater contact time between the gas and the catalyst for a given overall space velocity of the reacting gases.

The cold synthesis gas enters at one end of the converter and passes to the other through the space between the pressure shell and the wall of the cartridge. Next, it enters the tube side of the main heat exchangers; from there it passes, by way of a duct arranged concentrically around an axial gas inter tube, to the tube side of the second and subsequent intermediate heat exchangers. As it enters any or all of these heat exchangers, the gas temperature is adjusted by addition of cold synthesis gas introduced through the axial gas inlet tube or tubes, the number of which depends on the number of points at which the gas is to be introduced. After the final heat exchanger, the temperature of the synthesis gas is adjusted by adding cold gas, before it enters the first catalyst bed. It then passes sequentially through each catalyst bed and the shell side of the appropriate heat exchanger, finally giving up its heat to incoming synthesis gas in the main heat exchanger before passing out of the converter.

A theoretical comparison of the efficiency of the indirect and quench cooled converter concludes that the ammonia production of the OSW converter exceeds that of the quench converter in the proportion of 157/143. Undoubtedly, the performance of the indirect cooled reactor is better than that of the quench converter if the catalyst beds are of the same temperature in each case; because every time when quench gas is introduced, the ammonia concentration of the gas stream entering the subsequent catalyst bed is lowered. The quench converter designing also requires a different approach from that applicable to the design of the indirect cooled converter. Moreover, the quench converter needs more catalyst to produce ammonia at a given rate and for overall conversion efficiency than the indirect cooled OSW converter requires.

Steam Production: In the OSW system, steam is generated at 100 atm. pressure from the waste heat of ammonia synthesis gas from the converter, at 400°-450°C, by passing through a waste heat boiler and then into a heat exchanger. It is finally cooled in a water cooler before passing to the separation unit.

[*Nitrogen*, No. 81 January/February (1972), 29]

Material Selection Problems in the Ammonia Industry

Ammonia plants with 600 tpd capacity look very small these days as we find today one 1,700 tpd plant already in operation, while designs for 3,000 tpd plants are also available. But larger plants need to be more reliable in operation, as the cost penalty resulting from unplanned shut-downs is more severe than in smaller plants. With change in designs and process conditions, it has become necessary to re-evaluate material specifications for these modern ammonia plants regularly.

The pigtails have to be subjected to cold working during bending to give them their final conformation otherwise it can give rise to problems in operation. It is suggested, therefore, for service temperatures above 750°C, the pigtails should either be fully solution-annealed or, if this is not possible they should be designed with an additional safety margin of 1.3 or 1.4 to allow for the weakening caused by recrystallization. In case the pigtails are required to be used at higher temperatures, heat treatment after bending is definitely the most economical solution. However, if intended service temperature is less than 750°C, full solution annealing is advisable as an insurance against the risk of over-heating, ever-present in this kind of furnace.

An ammonia plant uses a number of heat exchangers and coolers which use water as a cooling medium. Majority of these are of shell and tube-type and in many cases, they are equipped with standard austenitic 18/8 steel tubes. This tube material falls prey to stress corrosion cracking after a good working for a number of years. This happens mainly due to the change in the quality of the cooling water which may contain chloride (*c*.50-500 ppm). As nothing could be done about the chloride content of the water supply, the remedy was found in replacing the original tubes with ones made of 3 RE 60.3 RE 60, with the following nominal composition (in wt%) is a development of well known AISI type 316L stainless steel and is specially designed to resist stress corrosion cracking.

C(max)	Si	Mn	P(max)
0.030	1.7	1.5	0.030
S(max)	Cr	Ni	Co
0.030	18.5	4.7	2.7

But neither of these materials (3RE 60 or 316 L) find any application if the cooling medium is sea water as they are susceptible to pitting at high chloride concentrations (2,000-45,000 ppm in sea water), Instead, the austenitic, extra-low-carbon (ELC) grade 2 RK65 steel (composition: 19.5% Cr, 25% Ni, 4.5% Mo & 1.5% Cu) should be used. Design equipment should also be made such so as to keep down the water flow rate to 1.5 m./sec. instead of the more usual rate of up to 3 m./sec.

In the modern plants, the high pressure steam which is used to drive the synthesis gas compressors is generated at about 100 atm. (1,420 psi) and 500°C as compared to a pressure of 15 atm. (210 psi) and the temperature about 200°C in older plants. These harsh conditions, however, place higher demands on the materials used in the construction of boilers. For this, the boiler material must possess the four essential qualities.

1. resistance to hydrogen attack,
2. resistance to Nitriding,
3. resistance to stress corrosion cracking from the water/steam side; and
4. high mechanical strength.

Keeping these essential qualities of the boiler materials in mind, the performance of five types of steel in respect of each characteristic are summarized in the following table (a + sign indicates satisfactory performance and a – sign unsatisfactory performance).

	Hydrogen attack	Nitriding	Stress corrosion cracking	Mechanical Properties
Carbon Steel	–	–	+	–
18/8 grades (AISI 304)	–	+	+	+
25/20 grades (AISI 310)	+	+	–	–
Sanicro 30 PWR	+	+	+	+
Alloy 600	–	+	+	–

Thus, Sanicro 30 (a modified alloy 800) satisfies all requirements in respect of its resistance to hydrogen attack, nitriding and stress corrosion cracking besides possessing high mechanical strength. This material has found its use for retubbing in a number of steam generators recently.

[*Nitrogen*, No. 82 March/April (1973), 31]

Science Policy

Under the joint auspices of the Unesco and CSIR a summer school on science policy studies in India was held at New Delhi from July 23 to 28 1973 with scientists from USA, U.K., Canada, FDR, GDR,

S. Korea, Indonesia, Sri Lanka, Afganistan, Bangladesh, Thailand and India participating. Inaugurating the school Sri S. Subramaniam, Minister for Industrial Development and Science and Technology, dwelt on the socio-political interactions of science at different stages of development of the country. The government attached much importance to the application of science and technology to the economic growth of the country and therefore it was but opportune that scientists were involved in framing a definitive policy and a plan of action within that framework for science and technology

Initiating the proceedings of the school, Dr. Y. Nayudamma, DGCSIR, announced the establishment of a cell for Science, Technology and Development in CSIR. In his remarks, Dr. Derek Price, Chairman of the International Commission on Science Policy Studies stated that India had decidely proved its competence in the field of science policy studies and was considered one of the pioneers in the field. In his opinion, there is adequate talent in the country but it was being underutilized. Some of the important papers presented at the school are the following: (1) Quantitative Methods in Science Policy Studies by Derek Price USA (2) Theoretical Problems of Science Policy Studies by G. Krober, USA, (3) International Scientific Cooperation, Foreign Policy and National Participation in International Scientific Cooperation by Brigitte Schroeder, Canada, (4) Science Policy and Participation in International Institutions by E. Skolnikoff USA, (5) The History of Social Studies of Science and Social Responsibility and the Scientists by Roy Macleod, UK, (6) Science Policy in Asia—Castasia with Reference to Hopes and Reality by B. D. Nagchaudhuri, (7) Role of Multinational Corporations by K. K. Subaramaniam, (8) Social and Cultural Factors in the Development of Science with Particular Reference to Developing Countries by S. C. Dube, (9) Role of Scientific Academic and Professional Bodies in Shaping Science Policies by B. V. Ranga Rao and (10) Country Reports on the Present Structure of Science and Technology, including Role of Agencies in Policy by delegates from Bangladesh, Indonesia, Korea, Sri Lanka and Thailand.

In his paper, entitled 'The Need for the Choice and Assessment of Technology', A. K. N. Reddy discussed the need for development of alternative technologies by the developing countries. Technologies were rarely available in advanced countries and hence would have to come out of indigenous efforts alone. The alternative technology should be capital and energy-saving and employment-generating; should promote cottage and small-scale production of goods of mass consumption; should require little skill or small modification in the skills of traditional craftsmen; should be based on local materials and local sources of energy; should lead to scaled down dispersible miniaturized factories and thus lead to symbiotic and mutually reinforcing dependence of metropolitan industry on the rural sector. Alternative technologies would not only lead to reduction of income disparities and improvement in the balance of payment but also have the following spin-off benefits: (i) would by-pass the most importent weakness of R and D institutions in developing countries; (ii) R and D bill for the development of alternative technologies was reasonably certain to be a small fraction of the cost of achieving self-reliance in classical capital and energy-intensive large-scale technologies; (iii) a commitment to alternative technologies would result in science and its methodology being brought to the rural populations. The resulting dissemination of the scientific temper would have far-reaching effects on social transformation.

A. Rahman discussed the problems of science and technology in the developing countries as seen by a research worker participating in the development of science. The perception of scientists and technologists in developing countries was narrow and lacking in critical analysis which inhibited science and technology taking roots in the developing countries. Scientific development is viewed in isolation from the social and political developments taking place. This compartmentalized approach led to imbalances.

The developing countries were also exposed to the pressure and fashions of the academic world of the developed countries. The vicious hold of the multinational corporations and dumping of obsolete technologies through the so-called benevolent programmes of technological aid and foreign collaboration helped increase confusion in the developing countries. These countries, therefore, needed to develop their science policy studies which could analyze each one of these aspects in depth and offer options to the decision maker. Science and technology at various intervals of time had stood up against the evils of feudal systems but the situations might not be the same in the modern world.

Some of the important recommendations made at the school were: (i) summer schools should be held once a year or two years (ii) delegates to these schools may be chosen from the students and administrators besides from those who are engaged in science policy studies; (iii) the summer schools should concern themselves with the problem of formulating a proper science policy and their promotion and implementation; (iv) in order to promote science policy studies, (a) suitable university level courses be prepared, (b) a half-yearly bulletin on science policy matters be issued, (c) association for promotion of social responsibilities among scientists be sponsored and (d) small working groups in science policy be formed in each country.

[*CSIR News*, **23** (18) (1973), 141]

Economic and Technological Factors in Large-sized Ammonia Plant Design

Designing a giant ammonia plant has become very necessary because of the increasing demand for fertilizer and ammonia-based chemicals. The improvements in machinery and vessel fabrication have resulted in the satisfactory performance of two plants having capacities in the range of 1,100-1,700 tpd. Because of the successful experience of these plants, new attention has been focussed on still larger single train plants with 2,000 tpd or even more capacities. Technically, there are no design obstacles that can't be overcome with respect to the giant plant but such an undertaking would certainly involve numerous problems and risks besides the huge initial investments and working capital factors. A qualitative analysis of some of the major factors involved in a giant plant undertaking need evaluation.

The first and the foremost factor which requires evaluation is the selection of the site for the plant. Selection of the site would essentially involve an evaluation of two major factors, both directly related to feed and fuel cost structure. A plant site near the source of feed would be linked with low investment and higher utility consumption while still retaining low operating cost barring, of course, any difficulties associated with intangible factors. On the other hand, a plant in a high feed cost area involves higher investment which is the result of designing for maximum heat recovery, efficient steam utilization, and the use of more efficient machinery. Despite high thermal and mechanical efficiency, production cost would still be high at this location largely because of overwhelmingly greater unit cost of feed and fuel. Stream efficiency, however, would be expected to be higher for this site selection.

Secondly, the producer may consider designing the unit on the basis of use of two half-size centrifugal compressors for critical process services, such as secondary reformer air and/or the synthesis gas recycle compression. This would ensure operation of the plant at about 50-60 per cent capacity in the event of difficulty in these major process areas. It may also be decided to use single 100 per cent centrifugal machines throughout the unit and to provide spare rotors for all compression services.

A producer, on the other hand, is generally reluctant to adopt untried techniques in the giant plant or equipment involved because of the risk factor and reasonable degree of uncertainty. So, the sequence of operations would involve the same design and proven techniques. On this basis, the over-all design would comprise desulphurization, primary and secondary reforming, high and low temperature shift conversion, removal of CO_2, methanation, compression and ammonia synthesis.

Before any design for a modern ammonia plant is established, three major interdependent process services need a careful evaluation. These are: hydrocarbon reforming, ammonia synthesis and high pressure steam generation. After examining the effect of variations of pressure on the design for each of the processes, certain conclusions can be drawn.

1. It will require an increase in reformer pressure to permit greater pressure drops in the raw gas generation and purification systems to limit pipe and equipment sizes and to avoid penalty in fuel consumption.

2. The operating pressure in the synthesis loop will have to be increased to higher levels in order to increase the conversion per pass and thus reduce gas circulation.

3. Higher recycle differential will be required in the synthesis loop to reduce the size of high pressure pipes and exchangers.

4. Higher steam generation pressures and superheat will accompany increases in reformer pressure for high fuel cost areas while no major changes will be required for low fuel cost areas.

5. There will be a utility penalty because of the necessity of having to design certain critical process areas for much higher pressure drops. However, this penalty may be nullified by the improved efficiency of compressors.

Above all, the present supply-demand situation is unlikely to favour the commissioning of such giant plants in the foreseeable future.

[*Nitrogen*, 80, (Nov./Dec.) (1972), 28 and 8, (Jan./Feb.) (1973), 32]

FCI Ltd. During 1972-73

Shri K. C. Sharma, Chairman & Managing Director, Fertilizer Corporation of India, gave a statement on the performances of the Corporation for the year 1972-73 on 26th December 1973 at the 17th Annual general meeting of the Corporation held at New Delhi.

During the year the Corporation made a gross profit of Rs. 19.92 crores which after providing Rs. 11.16 crores as depreciation and Rs. 3.34 crores as interest, resulted in a net profit of Rs. 5.42 crores as against last year's profit of Rs. 1.92 crores. The turn-over of the Corporation was Rs. 92 crores, which is three crores less than that in the previous year. This reduction in turnover was mainly due to non-availability of imported fertilizers from the Pool for the Seeding programme. Against an authorized capital of Rs. 400 crores, the Corporation's paid-up capital as on 31st March 1973 stood at Rs. 203.06 crores including advances thereto.

During the year, Trombay has considerably improved in production and made a record profit of Rs. 8.15 crores. Nangal made a profit of Rs. 3.49 crores despite a loss in profit of Rs. 2.3 crores sustained due to drastic power cuts imposed by Bhakra authorities. Gorakhpur has shown a profit of Rs. 0.25 crores while the Planning & Development Division's profit was Rs. 0.23 crores. The total profit of Rs. 12.12 crores made by these three operating units and the Planning & Development Division, however, has been reduced to Rs. 5.42 crores through the losses sustained at Sindri (Rs. 5.80 crores), Namrup (Rs. 0.53 crores) and the write-off amount of Rs. 0.37 crores as deferred revenue expenditure at the central office.

Adopting 50% of the gross fixed assets of production Units to represent equity of Rs. 203.06 crores the net operation profit of Rs. 5.42 crores for the Corporation works out to 5.5 per cent as compared to 1.9 per last year.

This year had also faced the continuous increases like last year in the cost of various inputs, viz. electricity, naptha, freight, labour, etc. whereas there had been no corresponding increase in the sale price of fertilizers, which in some cases, is statutorily controlled. Besides, there had also been serious production losses which were beyond the control of the Corporation on account of power cuts/power interruptions/voltage drops and low power frequency. These adverse factors eroded the Corporation's profit by about Rs. 40 crores. Further, the Corporation has paid to the government during the year Rs. 7 crores as excise duty on fertilizers. If the production capacity achieved be the index of operation efficiency then the performances of Corporation's different fertilizer factories have been quite impressive with Trombay unit attaining 91 per cent, Gorakhpur 86 per cent, Namrup 78 per cent, Nangal 68 per cent and Sindri 88 per cent. The overall utilization of the five units works out to about 83 per cent which could be considered reasonably good for the fertilizer industry. In Sindri unit though 88 per cent capacity production was attained during the year, the unit has incurred a loss of Rs. 5.8 crores, mainly because of fast deteriorating coke-oven batteries and gas plants and also due to inadequate supply of raw materials, like gypsum and coal. In order to improve the performance of this unit, certain measures have already been taken which include various renovations and repair programmes in respect of coke-oven batteries, etc., a Rationalization scheme to substitute the high cost natural gypsum from Rajasthan by the by-product gypsum and a Modernization scheme to replace the existing process of ammonia.

The marketing organization, already set up by the Corporation, covers practically the entire country for distributing fertilizers. Against the current level of production of Rs. 3.61 lakh tonnes of nitrogen from the existing five units, this organization is served with a big challenge for distributing larger quantities over the next 3 to 4 years when the fertilizer output in the existing as well as six new units increases to 20 lakh tonnes of nitrogen. The Corporation continued to pursue the policy of promoting sales through cooperatives and other institutional agencies besides strengthening the network of small dealers including educated unemployed youths and disabled exservicemen. Considering the inadequate fertilizer production in the country, the Corperation made some qualitative changes in its fertilizer promotion activities to lay stress on optimum use of fertilizer. The Corporation continued to impart in package its services to farmers through various media, viz. fertilizer demonstration in fields, soil testing services and farmer's education programmes like fertilizer festivals, field day seminars and training camps.

Currently, the Corporation has in hand eleven major projects, viz. Durgapur, Barauni, Namrup Expansion, Sindri Rationalization, Ramagundam, Talchar, Gorakhpur Expansion, Haldia, Nangal Expansion, Sindri Modernisation and Korba, which are in the various stages of execution, Another two projects to be taken up shortly, are Trombay Expansion and Paradeep. The Corporation has also prepared feasibility reports for joint venture projects in Kuwait and Bahrein and submitted to the concerned authorities.

After facing considerable difficulties in commissioning and consequently modification and replacements made at Durgapur, the plant started trial production of ammonia and urea in early October 1973. The plant, after operating in small spells, has been brought up to a 50 per cent production level. Certain measures for attaining stability in production have been drawn up and are under implementation.

The Corporation's approach to the construction of new projects continued to base on maximum indigenisation and self-reliance. In regard to indigenisation of feed-stock, Corporation has made notable contribution, as for instance, in the case of the three major projects at Ramagundam, Talchar and Korba based on coal technology. The importance of these projects based on indigenous raw material is highlighted and appreciated in the present context of non-availability of Naphtha and the uncertainly in crude oil supply position and their fluctuating prices in the international market on account of the energy crisis. The P & D Division of the corporation has developed sufficient expertise for design, engineering, procurement and installation of various projects. Further, it has been possible to establish progressively with various indigenous fabricators, fabricated capacity for production of more and more of sophisticated items which were previously imported. Thus, the price which the Corporation pays through increased cost and other difficulties and even delays, to attain its objective of growth through self-reliance, should be accepted as the unavoidable cost for National growth. To man its various Units and Projects, the Corporation has built up adequate capacity for training about 2200 personnel in the various fields of specialisation.

Control of Urea Dust Pollution

The origin of urea dust is atomized molten urea and undersized or crushed prills. Both sizes of dust can cause air-pollution resulting in direct harm to plants or low visibility. One of the measures for control of the emission of urea dust in air is an impinger-type device with baffle plate and water curtain system. This system is simple and effective for relatively larger size of particles, which are easy otherwise to separate by the gravitational sedimentation, and requires very small pressure drop. Thus, it is essential to evolve such a system which has maximum collection efficiency with minimum pressure drop. In an effort to determine the most effective and suitable de-dusting system, a spray tower, a packed column, and a cyclone scrubber were investigated. In each case a highly effective moist eliminator was required to reduce the fine mist which accompanied the air stream. Based on a series of trials, the proceedure selected was as follows:

The air stream containing urea dust is introduced into the bottom of a column equipped with a spray nozzle and filter type mist eliminator in series through guide vanes. A resin foam filter is installed either horizontally, vertically or out of perpendicular. The solution is passed through the filter and accumulated at the downstream side, and extracted out of the system or collected in the sump through a down comer pipe. For the control of the system, an orifice, rotor meter and inclined-tube amanometers are provided. The following design basis has been recommended to achieve a dust content of 30 mg/std.cu.m. at the scrubber exit.

Flow rate of air 500,000 std.cu.m/hr

$\frac{\text{Flow rate of liquid}}{\text{Gas flow rate}}$ ratio (L/G), 1.5-.201/std/cu.m

Efficiency in spray section 90-96%

Efficiency in total or overall 95-99%

This system has been used in a 1,000 metric ton/day plant in Japan with similar operating efficiency.

Furthermore, an ammonium nitrate scrubber handling almost 800,000 cu.m/hr of air has also been designed on the similar lines because this principle holds good to any water-soluble material. In addition, both the investment and operating costs of this system are far lower than those of other type of scrubbers with a similar dust collection efficiency, such as wet-cottrell and the disintegrator.

[*Chem. Engng Prog.*, **69** (6) (1973), 72]

SO_2-Pollution in Sulphuric Acid Plants

In the basic fertilizer industry, atmospheric pollution created by vented gas from sulphuric acid, phosphoric acid and nitric acid plants is common. A major pollutant is sulphur dioxide gas, which is released from sulphuric acid plants as well as from power generating plants using fuel with sulphur impurities. In certain concentration SO_2 has measurable detrimental effects, and the control of its concentration at ground level in the vicinity of sources has, therefore, constituted a great step forward in our environmental control. However, there is a strong evidence that half life of SO_2 in the atmosphere is at the most two days, more probably a few hours and further that nature runs a marvelous, SO_2 clean-up plant consisting of a mixture in unknown proportions, of oxidation to SO_3 by ozone or by catalytic action of particulate matter, reaction with atmospheric ammonia or with alkaline particulate matter, and scrubbing by rain, snow and sleet. In spite of it, man has employed costly processes for the removal of SO_2.

Economic recovery is not always possible, but this is no longer a criterion to justify industrial use. In sulphuric acid plants the double-absorption system is being increasingly adopted to reduce the SO_2 concentrations vented to the atmosphere. Originally, this system was developed in the mid 1960s in Germany, but now plants built in Australia, Belgium, Japan, the United Kingdom and United States use this process.

Another approach is the pressure process for sulphuric acid plants whereby after drying the air, the dried air is compressed to 3.5-6.0 atm. But this process is not considered thermally efficient as the standard sulphuric-acid plant operates close to atmospheric pressure.

Tail-gas treatment coupled with absorption by-product has been considered and adopted for sulphuric-acid plants in Czechoslovakia, Rumania and the United States. A single stage scrubbing can reduce the SO_2 concentration to between 500 and 800 ppm in the tail gas. The scrubbing can be done with the addition of ammonia, resulting in the formation of ammonium sulphate solution; by adding sulphuric acid, this is converted to ammonium sulphate and SO_2. The addition of ammonia can be controlled by pH.

A magnesium-oxide scrubbing process, with regeneration of SO_2, has been developed in connection with a power-plant project in the United States. Absorption on solid adsorbants is being studied for SO_2, but this process is still in the development stage.

Solution-scrubbing methods do not normally remove acid mist. Mechanical means using filtration are available but allowance has to be made for their relatively high-pressure drop.

Potential for Synthetic Oil

The steady rise in the price of the natural crude by OPEC countries has forced the scientists to find out the possibilities of commercial production of synthetic liquid fuel from tar sands, shale and coal, We do not have tar sands and shale but we do have large reserves of coal. Recently M. W. Clegg, B. P. has pointed out to these new sources of oil some of the technical, logistical problems relating to its commercial production.

Though it is too early to assess the realistic recovery factors for these raw materials yet even a very low recovery rate would provide a potential supply of synthetic oil many times greater than the world's proven recoverable reserves of conventional crude of 673 billion barrels. To quote an estimate; even a very low discovery factor of 10 per cent applied to the world's estimated coal reserves of 9,000 billion tons would mean potential reserves equivalent to 4,300 billion barrels of synthetic oil, which is well over six times the comparable figure for conventional crude at present.

Exploiting these resources will, however, be a considerably more complex operation than that used in a conventional oil field. For example, the commercial production of synthetic liquid fuels from coal will require the development of new technologies for hydrogenation and the manufacture of hydrogen from coal (with steam) or coal-derived material, plus efficient catalysts to work at the very high temperatures and pressures needed in the hydrogenation phase.

As a step towards self-sufficiency, the U.S. Office of Coal Research (OCR) is supporting a number of coal liquefaction pilot projects, viz. solvent refined coal process, H-Coal hydrogenation process and COED (Char Oil Energy Development) plant based on pyrolysis. The oil yield varies substantially with the process, e.g. for H-coal hydrogenation process, it is estimated at 3.6 barrels of oil per ton of coal whereas COED plant yields only 1.4 barrels per ton. While assessing the future of synthetic crude production the author suggests that liquefaction of coal is likely to remain the most expensive source of oil and therefore, may not be developed, although a figure of 80,000 b/d for U.S. capacity by 1985, is quite reasonable. The alternate sources such as shale and tar sands, which are less expensive, would be preferred for the production of synthetic oil.

Taking account of all operating and financing costs, Mr. Clegg estimates that synthetic crude would have to sell for at least \$ 5 to \$ 7 per barrel in the USA, and even more in western Europe and Japan because of greater transport costs from the source of supply. The author, however, suggests that positive steps should be taken to expand the present research and development effort and also that some governmental cooperation and financial assistance will clearly be needed to step up the pace.

[*Oil Commentary*, **9** (3) (1973), 1-4]

Recent Developments in the World Fertilizer Supply and Price Situation

Prices of fertilizer in the international market depend on supplies and demand and their reasons are complex. In the late 1960s, the excess capacity was the result of earlier investment in new plants by the traditional fertilizer export producers and the entry of petroleum companies into the fertilizer industry in the expectation that demand for fertilizers would increase rapidly in the developing countries. At the same time, as a result of breakthroughs in technology the economic size of nitrogen plants, for example increased from 300 tons of ammonia per day to 600, 1,000 and now to 2,000 tons or more. These developments led to larger supplies resulting in downward trend in fertilizer prices. Even though fertilizer consumption was rising by about 15 per cent a year in the developing regions and by about 8 per cent in the developed ones, this did not absorb the large increase in output made possible by the bigger plants and large stocks were therefore built up. But then some oil companies withdrew from the production of fertilizers, traditional producers closed older uneconomic units and production controls were introduced in certain sectors. Some new capacity plants specially in developing countries failed to reach expected levels of production due to various reasons. On the other hand, demand for all three nutrients nitrogen, phosphate and potash has continued to grow steadily. From the latter part of 1971 supplies of fertilizer in the international market became short and prices started to rise. Over the longer term fertilizer prices have risen much less than those of other purchased farm inputs. However, in the future rising cost of raw material (particularly natural gas and petroleum feedstocks) and of pollution control may adversely affect the prices of fertilizers. At psesent there is a tight balance in the word supply and demand of nitrogen fertilizers and also in the case of phosphate and potash fertilizers.

In 1971/72 the developed countries accounted for just over 80 per cent of all fertilizer consumption; nitrogen, by far the most widely used fertilizer, represented 47 per cent of world consumption compared to 29 per cent for phosphate and 24 per cent for potash. Owing to the location of its deposits, potash accounted for 50 per cent of world exports, nitrogen 34 and phosphate 16 per cent. Developing countries relied on imports for 55 per cent of their supplies of all three nutrients. In 1971-72 fertilizer year the producers were only meeting known requirements and not building stocks of fertilizers. Urea in recent years has become the leading nitrogen product accounting for over 40 per cent of trade in nitrogen fertilizers in 1971, was in short supply as well as ammonium sulphate, which however owing to low nitrogen content has become relatively less important. The tight supply situation of fertilizers resulted in a higher price. In the first quarter of 1973 prices were beginning to level off and price increase was at reduced rate. Urea prices per ton from west European f.o.b. rose to \$ 50-55 from \$ 40-46 in one year during 1971-72. Prices f.o.b. Japan also rose to \$ 70-75 per ton by the end of 1972.

Phosphate and potash fertilizers have registered increases in price during 1971-72. The adjustment of international currency values has coincided with the increased fertilizer prices. For most exporting countries which traditionally quote their prices in dollars the devaluations of 1971 and early 1973 will reduce return and may result in further compensatory price increase. The ex-factory prices of locally produced fertilizers in some developing countries are higher than those for imported materials because of the higher costs of domestic production. In the next year or so changes in Indian and Chinese procurement plans are likely to be a major influence on export market. The imports of these two countries account for about 30 per cent of the total volume of nitrogen in international trade. While they produce under 8 per cent of the world nitrogen supply, they consume 15 per cent.

India, which now has a production capacity of about 1.8 million tons of nitrogen, is making a determined attempt to reach an output of at least 1.3 m. tons in 1972/73 by improving capacity utilization rates which averaged about 60 per cent in 1971/72. To meet its requirements of some 3.8 million tons of nutrients in 1973/74, India will have to import large quantities of nitrogen, phosphate and potash fertilizers. It is expected that in the medium term it will have to continue to import at least 40 per cent of its requirements to meet demand in spite of the efforts being made to increase domestic production.

Fertilizer production in China in 1971/72 is estimated to be 2.83 million tons of nutrients of which nitrogen accounted for 1.84 million tons. Imports of about 1.6 m. tons were smaller than the year before when they totalled 1.8 m. tons of nutrients.

The overall picture gives every indication that supply and demand will remain in close balance during the rest of 1973. Prospects upto 1975 depend on the additional capacity scheduled to begin production in the near future, especially the large export-oriented manufacturing capacity in Eastern Europe.

Traditional exporters of fertilizers will probably be more hesitant about committing capital to new production capacity especially in the light of increasing cost and uncertain supply of petroleum feedstocks.

[*Monthly Bulletin of Agricultural Economics & Statistics*, FAO, **22** (6) (1973), 1]

Space Science Aids Agriculture

From 570 miles up of Erst I satellite launched by NASA perspective on agricultural situation was obtained. Investigators used the satellite to map crops, monitor crop conditions, survey and classify soil and inventory land use. As fall approached last year, observers could note a brown wave from north to south as the crops matured. A green wave from south to north was noted this spring as new crops began to grow. Aerial photographs have been extremely valuable to agriculture for many years and since 1940's aerial photographs have been used as a base for mapping soils. The cost of fuel and pay for a pilot of a plane would be prohibitive for aerial photographing, but a satellite could do it relatively cheaply. New technology allowed the development of a scanning device to replace camera and film. The development of high speed electromic computers provided a tool for reading and analyzing the information from the scanning devices and ushered in an entirely new age in remote sensing. Many agricultural problems have been studied with scanning and computers. Scientists in 1970 and 1971 were able to trace the spread of Southern corn leaf blight. Each individual image from the satellite covers an area on the earth's surface that measures 115 miles by 115 miles. Parts of these images can be enlarged to give a closer look at a particular area. If there is good contrast, it is possible to see things as small as 30 to 40 feet wide in these images. It is, therefore, possible to look at individual farm fields with quite a bit of clarity. The satellite records the data on magnetic tape, then transmits it when it again comes within range of a station. From different stations the data are transmitted to the Goddard space flight Centre at Green belt Maryland. From there the data in the form of black and white photos, colour photos or computer tapes are disseminated to more than 300 principal investigators around the world. These photos are not actually taken from the satellite, but are simultated photos produced from the digitized data received from the spectral scanner on the satellite. The satellite does not obtain photos directly. From the information thus obtained the changes in season, planting and growth of crops, the development and spread of disease, harvesting progress and many other things can be said. Satellite data can be used to delineate boundaries between different soils and to sort out other geological features.

[*Crops and Soils*, **25** (8) (1973), 18]

Top Dressing is Valuable on Small Grains

The practice of applying fertilizer to the field surface after seeding is a useful technique in small grain production. Earl Adams, an extension soils specialist at South Dakota State University, says that fertilizers dry or liquid high in nitrogen are to be used. The nitrogen will move downward through the soil with the moisture into the root zone of the small grain. Phosphorus and potassium will not move downward this way; therefore, fertilizers containing these two nutrients should be applied before or during planting. Nitrogenous fertilizers should be topdressed after planting of seedlings and cause minimum damage to them. The earlier the application, the more time the fertilizer will have to move down to the root zone for crop uptake. If little or no rain falls after the topdressing there may be little effect on the yield. Nitrogen applications made at the grain entering boot stage or later will frequently do very little to increase yield. Late applications, however will frequently increase plant nitrogen or grain potential levels. 30 to 50 pounds of actual nitrogen per acre are recommended for continuous cropped dryland fields and 20 to 30 pounds of actual nitrogen for fallow if soils tests have shown the nitrogen supplying ability of the soil is low. A sound weed control programme along with wise fertilizer use should be made to check the growth of weeds.

[*Crops & Soils*, **25** (8) (1973), 26]

Rice Production Training Institute, Durgapur

The Extension Worker is the kingpin to attain success in new agricultural strategy. He is the one who is exposed to the farmers and through the Extension Worker, the transfer of technology for cultivation of the new high yielding variety has to take place. Therefore, the success in the new agricultural strategy would depend very much on the success of the Extension Worker in making the technology transfer effective.

The concepts, plans and programmes formulated at national, state, regional, district and block levels by scientists, economists, administrators and experts for an all-round improvement in agricultural production through the medium of the new agricultural technology would only succeed if the Extension Worker functions effectively. It was felt that an Industrial Training Institute, imparting systematic practical training to the extension worker who would man massive extension and promotional programme spread all over India, is essential. While travelling from Australia to Japan via Manila, Dr. S. K. Mukherjee, Director, Fertilizer Corporation of India Ltd., visited the International Rice Research Institute (IRRI) and was impressed with the concept behind the Rice Production Training Programme at the IRRI. He reviewed with interest the young Philippine Extension workers undergoing a training of four months and actually performing each task from seeding to harvest to grow a crop of rice in a field.

Every operation has to be planned and performed inclusive of manual labour by the Extension Workers themselves. Such background of practical training equips the Extension Worker with appreciation of the problems of the farmer which would enable him to effectively communicate with the farmer. Concurrently, with such practical experience of growing a crop of paddy, the Extension Workers are given academic training in order that not only "know-how" is imparted but also "know-how" behind the various operations that are systematically undertaken to successfully grow a crop of rice.

This prompted Dr. Mukherjee to start Rice Production Training Programme in India on the lines of IRRI. Four young Agricultural Scientists from FCI were deputed for six months training at Manila. This formed the nucleus. The choice of site fell on Durgapur for obvious reasons; Burdwan district in West Bengal is practically exclusively paddy growing and one of the districts selected for the Intensive Agricultural District Programme.

The Rice Production Training Institute was formally inaugurated on 30th June, 1972. The first batch of 19 trainees from the States of Bihar, West Bengal, Assam and Tripura successfully underwent training for four months This training programme is basically field oriented with objective to expose the trainees to first hand practicals in different aspects of rice culture. The field programme is supplemented with class room lectures in the different disciplines of rice culture.

In field activities the following projects are allotted to the trainees.

1. *Production Plots*: The varieties, Vijaya, IR 20, Jaya, IET 1991 are grown with a view (i) to explore the maximum yield potential of variety under optimum management conditions (ii) to gain experience by actually performing all the necessary operations associated with rice production and (iii) to take note of some economic aspects of rice production.

2. *Varietal display plots*: 17 varieties were grown: (i) to determine the growth duration of these varieties under Durgapur condition and (ii) to collect data on the performance of these varieties/selections with reference to their particular fertilizer recommendations and cultural practices.

3. *Project Plots*: The objective is to conduct experiments on different aspects of rice culture. (a) **Nitrogen-cum-variety**—In this project four levels of nitrogen (0:40:80:120 kg/ha) are tried with three varieties—Jaya, Vijaya and IR-20. The objective of this project is (i) to study the effects of four levels of nitrogen on yield potential of three varieties (ii) to find out the optimum levels of N for each variety under study and (iii) to find out the effects of nitrogen levels on the yield components of three varieties.

(b) **Stand establishment trial**—Broad casting, direct seedling in lines, transplanting (Dapog seedling and wet seedbed seedling) in varieties (Pusa 2-21 and Bala) with N:P:K-100:60:60 kg/ha the project was studied with an objective to find out the best method of stand establishment under conditions prevailing at Durgapur Farm.

(c) **Variety-cum-number of seedlings**—Three varieties, Cauvery, Ratna and Bala, are grown under 2, 4, 6 and 8 seedlings per hill (N.P.K-100:60:60 kg/ha) with an objective (i) to indicate optimum number of seedlings for maximum yield of these varieties (ii) to study the effects of number of seedlings on yield components.

(d) **Granular insecticides**—In this experiment five granular insecticides at the rate of 1.5 kg./ha are tried against the control on the variety Jaya. (N:P:K-120:60:30 kg./ha). The objective of this project is (i) to test the efficiency of different insecticides against insects, attacking paddy and (ii) to demonstrate the maximisation of yield potential of a variety of controlling insect pests.

Besides this a 50 acre training-cum-experimental farm is under development. This year about 20 acres in the farm have been covered under different varieties of paddy. As at present there is no irrigation provision in this farm for which only one crop is raised during the kharif season. With the assurance of irrigation, intensive cropping would be possible.

National Committee on Science and Technology (NCST)

Out of the various proposals* submitted to NCST the following proposals were approved by NCST Panel V, Planning Group II on 'Fertilizers and Other Plant Nutrients'.

1. High pressure gasification of solid fuels for direct manufacture of Ammonia/Methanol/Oxo synthesis gas. (2) Intensive development work on the determination of suitability of different types of rock phosphate resources in India for production of phosphatic fertilizers. (3) To develop a technique for reuse of byproduct phosphogypsum for recovery of sulphuric acid and cement. (4) Recovery of sulphur from by-product phosphogypsum. (5) Extraction of phosphoric acid from rock phosphate using ammonium sulphate in a cycle. (6) Utilization of pyrite cinder obtained as by-product from pyrite based sulphuric acid plants. (7) Recovery of fluorine from fluorine bearing wastes of phosphate fertilizer and chemical industries. (8) Hydrazine cracking catalyst. (9) Development of a suitable substitute of platinum catalyst for oxidation of ammonia to nitric acid. (10) Hydrofining catalyst based on indigenous raw materials. (11) Preparation of superphosphoric acid and ammonium polyphosphate. (12) Development of a comprehensive process for the production of different types of alumina and aluminium compounds required for industrial uses. (13) Development of Deoxo catalyst based on indigenous raw materials. (14) Prereforming catalyst. (15) Development of a new technique of remote control of electrical capacitances. (16) Design and fabrication of an instrument for rapid non-destructive estimation of ferrite in austenitic stainless steels. (17) Development of advanced nondestructive testing techniques for evaluation of engineering materials and plant equipment related to fertilizer and heavy chemical industries. (18) Pressure vessel evaluation by experimental stress analysis under simulated loading. (19) Evaluation of service defects on a few specific equipments of fertilizer/chemical plant by specially developed NDT techniques. (20) Studies on vibration levels associated with service deteriorations of high speed rotary machines and related equipment used in fertilizer/heavy chemical industry. (21) High priority work on the direct application of ammonia as fertilizer into soil. (22) Beneficiation of low grade rock phosphate. (23) Studies on and development of nitrification inhibitors for soil application. (24) Simultation and on-line optimal control of an ammonia plant. (25) Development of pilot plants for mass culture of blue-green algae. (26) Use of ammonium bicarbonate as a fertilizer. (27) Utilization of fly ash.

The following R & D proposals were not approved. (1) Development work on a thermal (fuel intensive) method for release of phosphorus from low grade Indian rocks. (2) Production of phosphoric acid from rock phosphate using nitric acid. (3) Possibilities of regeneration of nitric acid from by-product calcium nitrate. (4) Possibilities of separating excess ammonium nitrate from nitrophosphate to produce balanced grade of NP fertilizer. (5) Development of a suitable catalyst for conversion of low boiling hydrocarbons into methane rich gas. (6) Encapsulation of technology for timed administration of plant nutrients and protectives.

The following proposals on the gasification of coals were reviewed: (1) Feasibility of hydrogasification of coal under pressure for the production of pipelined gas. (C.F.R.I.). (2) Feasibility of using CO_2 acceptor process for gasification of low rank, high ash, high moisture coals of India. (C.F.R.I.). (3) High pressure hydrogasification of coals for production of methane rich gas and high pressure hydrogen. (F.C.I.). (4) High pressure gasification of solid fuels for direct manufacture

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Technol.*, Vol. **9 (4) (1972), 445.

of ammonia/methanol/oxo synthesis gas (F.C.I.). (5) Development of an alternative reduction oxidation of iron oxide with producer gas and steam under fluid bed system and under pressure. (C.F.R.I.).

While discussing proposal No. 2, it was noted that experience abroad indicates that there are practical difficulties in applying this process to the gasification of coals other than lignite and hence it was felt that the process is restricted in its applicability. It is, therefore, not of immediate importance to the country and it need not be pursued presently.

The two research and development proposals, No. 3 from F.C.I. and No. 2 from C.F.R.I., deal with nearly the same technology. Since F.C.I. has better facilities for this type of work, the research and development work on gasification of coals may be initiated at F.C.I. and C.F.R.I. may consider associating with this R & D work in whatever manner they deem fit. There are several steps involved in this process which require in extensive research and development work, e.g. production of hydrogen, hydrogasification of coals, methanation of carbon monoxide-rich gas, etc. All these related developmental work need not necessarily be carried out at the same place. The research and development work in respect of proposal entitled 'Development of an alternative reduction oxidation of iron oxide with producer gas and steam in fluid bed system and under pressure' from C.F.R.I., for instance, falls in this category. It could be pursued independently by C.F.R.I. In the course of the discussions it was also pointed out that R.R.L., Hyderabad, has facilities for high pressure gasification of coals which can also be extended to include methanation of carbon monoxide rich gas. It is, however, essential that all the organisations taking part in different aspects of gasification of coals should work in close coordination.

Award

Sri Gurudas Mitra, Technologist (Gas Chromatography Laboratory, Chemical Research Wing, Planning and Development Division, Fertilizer Corporation of India Ltd.) has been awarded Ph.D degree in Chemistry by the University of Ranchi in May 1973, for his thesis, Gas Chromatographic Separation Characteristics of Hydrocarbons in Synthetic and Natural Products, under the guidance of Dr. N. C. Saha, Assistant Superintendent of this division.

Efficient utilization of petroleum and coal is ultimately associated with its detailed and reliable analysis of hydrocarbon components. The analysis of such complex samples for individual component is practically impossible by the conventional analytical techniques as there are more than a few hundreds of hydrocarbon components of various structural types, superimposed with the complexities of innumerable homologues and isomers in widely varying composition.

Undoubtedly, gas chromatography is the best technique today for such complicated analysis because of its proved safest and fastest method which involves problems of sensitivity and separation capacity. In spite of the spectacular advances of this technique during last fifteen years or so, many problems are still there in the separation and identification of complex hydrocarbon mixture in petroleum products. Work along this line in positive characterization of hydrocarbon component in petroleum is of course limited because of the following facts: (i) non-availability of pure reference hydrocarbons and their retention data; (ii) various types of hydrocarbon components having similar retention behaviour resulting in ambiguity in separation and identification; (iii) non-availability of retention data for solutes in any required stationary phase and column temperature; (iv) unclean preparative fraction according to carbon number or structural types; (v) non-reproducibility of retention data; (vi) conflicting views regarding mode of variations of retention parameter with column temperature; and (vii) non-availability of highly efficient columns. Thus, the development of some improved methods of analysis of complex hydrocarbon mixture will be an important practical solution to the industry dealing with petroleum as a raw material intermediate and finished product.

Arithmetic index has been proposed as an essential parameter, complementary to retention index. Comparison and interconversion of the two index systems and their correlation with the slope of the plot of logarithm of retention against carbon number of normal paraffins have been highlighted.

Correlation of retention index of solutes and nature of stationary liquid and column temperature have been focussed in order to make data readily available for systematic identification. Several graphical and mathematical relations have been established for this purpose.

A theory has been put forward stating that retention index varies linearly with column temperature in the full working thermal range, irrespective of the nature of the solute, substrate and forms of chromatography. The temperature coefficient of retention index (dI/dT) has been shown to be a new identification parameter in gas chromatography. The deficiencies of the use of single liquid phase have been removed by employing a pair of non-polar and polar liquids. The former effects separation according to vapour pressure and the latter predominantly according to structural differential of the solute molecule. The difference of retention index data in the two stationary liquids ($\triangle$I) and dI/dT being the basis of extended concept of Kovats retention index, has been successfully utilized in characterizing 200 hydrocarbons of various structural types in Indian petroleum naphtha.

The prediction of retention index from molecular structure and *vice versa* which will constitute a real break-through in the technique of identification by GC has also been explored.

The thesis of Dr. Mitra aims at amplifying and sharpening the identification power of gas chromatography. It represents, in general, an important contribution to the field of gas chromatography and particularly to the question of retention index concept and its applicability as identification parameter originally proposed by Kovats. His investigations are systematic and very thorough having independent thinking and particularly the ability of evaluating retention data published by others and of being able to draw original conclusions and new theories on its basis. Particular reference may be made to his very detailed studies and conclusions concerning the temperature relationship of retention index and the use of $\triangle$I and dI/dT for substance characterization and identification.

The analysis of Indian petroleum naphtha, by using the proposed method of Dr. Mitra, has been appreciated by internationally reputed gas chromatographers. The major advantage of the method together with sound and correct basis, is its simplicity and low cost.

Advanced work has been carried out in his laboratory on the extended concept of retention index system, which has been successfully applied in analysing kerosene fraction of petroleum. A paper on this topic has been presented by Dr. Mitra in the 4th International Symposium on Advances and Utilization of chromatography held at Bratislava (Czechoslovakia) during September 25-27, 1973. Although the findings in his thesis have been predominantly illustrated with hydrocarbons are nevertheless applicable to other types of complex samples.

News in Brief

US Boosts Coal Research

The US Government has awarded four contracts and extended one new one for power generation from coal.

Outlay will be more than $ 9 million under contracts with Pope, Evans & Robbins, C.F. Braun & Co., Combustion Engineering, Ralph M. Parsons, and STD Research Corp.

Fluidized-bed Boiler: The Pope firm of New York, received a $ 5.8 million 4-year contract from the Office of Coal Research (OCR) covering development of a 30-mw, coal-fired, fluidized-bed boiler. The boiler would burn high-sulphur coals within acceptable legal limits on sulphur and nitrous oxide emissions.

The pilot fluidized-bed unit is expected to burn coals with a wide range of Btu, moisture and volatile matter content, and without slagging problems.

Coal Gasification: OCR also has a $ 2.6 million contract to Braun for technical assistance in its coal gasification programme.

The 34-month contract calls for engineering support in evaluating OCR-sponsored processes to produce pipeline-quality gas from coal. Braun will help select process and preliminary design for a demonstration plant.

Another OCR contract to Combustion Engineering involves development of a gas-from-coal system. The initial phase of the contract will be to develop a system to produce low-sulphur, low-Btu gas for utility use.

Work will be done jointly by the company's Combustion Division and Lummus' subsidiary. Consolidated Edison of New York also will participate to evaluate the system for utility electric-power generation.

Fuel/Power Plant: A department of the Interior contract with Parsons covers engineering and technical evaluation services for OCR programmes. Parsons will perform an engineering and economic evaluation of candidate processes for reliable production of clean liquid or solid fuel from coal.

The Study will include production of gas, oil, and power in a single plant where output could be varied to suit regional coal resources and demand.

Total cost of the 4-year contract is estimated at $ 736,740. Parsons will contribute about one-third of the cost. *MHD Power*: OCR has increased its contract with STD on magnetohydrodynamic power generation from coal. STD has been developing a highly sophisticated mathematical model of MHD channel phenomena, OCR said.

[*Oil Commentary*, **11** (1) (1973), 12]

CSIR During 5th Plan Period

The basic philosophy of the CSIR's Fifth Plan is two-fold: work at its laboratories should form part of the total science and technology plan of the country and fulfil the national objective. The priorities and goals of the science plan in each sector will be formed in the light of priorities and goals of the economic and social plan for that sector. The emphasis in the national laboratories will be on generating employment opportunities for the scientists and attaining self-reliance in those areas of technology wherein the laboratories have already reached levels of proven competence.

CSIR, which has already over 40 laboratories under it, has indicated the need for additional 30 more institutes and about 50 research centres including 10 computer centres in the next five years. The research centres will functiou initially as autonomous units within the framework of the laboratories to which they will be attached, but they are expected to become full fledged independent centres. The proposal of an institutional nature will cover areas hitherto left relatively untouched, like paper and pulp, refrigeration and air-conditioning and solar energy. Besides these institutes, some regional research laboratories and polytechnological clinics may also be set up.

In the selection of research projects, the socio-economic importance of a project, its quick-yielding potential and its impact on society will have to be judged. The scheme will then be presented for consideration of the National Committee on Science and Technology and the Planning Commission. If the thinking of all the three organizations coincides, it will be get national priority. If an industry displays interest in a particular project, the CSIR will gladly give the necessary special priority to it but the cost will be shared by the concerned industry.

To help generate employment opportunities, the CSIR had drawn up a scheme for scientists and technologists for setting up their own establishments as entrepreneurs or as consultant agencies. A programme has been initiated to help entrepreneurs in developing production methods based on CSIR research. It is proposed to establish science-based industrial parks and polytechnological clinics, which will help in the formation of focal points around which industries will be activated.

CSIR proposes to enter the realm of housing, construction of roads, sanitation control and development of ground and mineral water resources. The Central Building Research Institute, Roorkee, has built over 1000 school buildings 20 per cent cheaper and 30 per cent quicker. This institute is developing designs for homes for middle income group people which are functionally useful, aesthetically appealing and cost-wise economical.

To establish an interface between the laboratories and the industries, CSIR also proposes to strengthen its industrial technological and scientific information service and undertake industrial surveys, marketing, economic evaluation and promotions of research and development. It also proposes dissemination of information and popularization of science in regional lauguages.

Import of Fertilizers and Fertilizer Raw Materials

Two recently held annual international conferences–one by the International Superphosphate and Compound Manufacturers Association at Rome and the other the Fertilizer Marketing Conference by the Fertilizer Institute of USA at Greenbier —provide an opportunity for assessing the prospects availability of fertilizers and raw materials in the international market.

Shortage of gas in the USA and the rising prices of petroleum feedstock all over have created a sense of uncertainty. The problem of pollution and the need for environmental protection is likely to act as a deterrent to any large-scale expansion of nitrogenous capacity in many of the developed countries. Meanwhile, in the developing countries the demand for fertilizers is increasing and the new capacity that may be created there will be barely enough to meet their needs. The developing countries can not therefore expect any increased availability of nitrogenous fertilizers from the developed countries. In fact, USA, India and China have imported some urea from the Scandinavian countries. The developing countries therefore have to look to alternative sources to meet their requirements such as Comecon countries. Japan, Middle East, Mid-eastern countries have vast resources of gas, on which developing countries, like India, can base their manufacturing facilities. India could develop with mid-eastern countries joint ventures for intermediates or finished products with an option on a part of the end-product by offering technicial know-how, plant and equipment and above all an assured market.

Many new phosphate fertilizer plants are under construction in Europe and USA and therefore availability of finished products should improve by 1975 when prices should also level off. Even then enough material may not be available to meet the growing demand of developing countries.

Regarding rock phosphate the diminishing reserves of the high grade ore will result in 'run of the mill' material being available. Therefore, there will be need for more investment to augment production and to open up more difficult deposits. Coupled with the cost of providing anti-pollution measures, a price of $ 15/te ex-mine is considered the lowest acceptable price. Sahara and Australia will be the likely sources for the supply of rock phosphate.

[*Fertilizer News*, **18** (7) (1973), 10 and 41]

Patents*

Ammonia Synthesis

Alexander Harmens (to Petrocarbon Developments Ltd.).
U.S. 3,666,415, May 30,1972, Brit. Appl. Sept. 30, 1969; 4 pp.

In NH_3 synthesis using He-containing natural gas as the source of the synthesis gas mixture an improvement consists of withdrawing a purge gas stream from the recycled gases. The purge gas is treated by low-temperature condensation to remove CH_4 and Ar, followed by treatment to remove He. The purified purge gas is then recycled to the NH_3 synthesis reactor.

[*Fertilizer Abstracts*, **5** (9) (1972), 219]

Ammonia Synthesis Catalysts

R. L. Burnett (Chevron Research Co.).
U.S. 3,653,831, Apr. 4, 1972, Appl. Oct. 4, 1968; 5 pp.

An NH_3 synthesis catalyst comprised of Fe, Al_2O_3, and Rb_2O with Fe/Al/Rb atomic ratio 100:5.3:2.7, and containing 1% Pt gave$\sim$9 and $\sim$16% NH_3 at 750 and 900°F, respectively, for a mixture with initial H_2/N_2 mole ratio 3:1 at 2500 psig and space velocity 40,000 standard vols of gas/hr/vol of catalyst. The NH_3 yield of the improved Pt-containing catalyst was higher than the yields obtained for a number of commercially available catalysts.

[*Fertilizer Abstracts*, **5** 9), (1972), 219]

Non-Caking Urea

Jean Cluzel and Paul Souviron (to Azote et Produits Chimiques S.A.).
U.S. 3,661,985, May 9, 1972, Appl. France Jan. 2, 1968; 2 pp.

Urea granules low in biuret (for example, 0.4%) and containing 0.9-1.2% H_2O and 600-1000 ppm NH_3 are sprayed with an aqueous solution of formaldehyde while maintaining the temperature at 0-50°. The spray solution contains 32-42% formaldehyde acidified to pH 3-4.5 with dilute HNO_3. The treatment results in a film of hexamethylene tetramine formed *in situ*.

[*Fertilizer Abstracts*, **5** (9), (1972), 220]

Corrosion Inhibitor for Ammoniated Superphosphoric Acid

H. F. Scott (to Allied Chemical Corp.).
U.S. 3,630,752, Dec. 28, 1971, Appl. Sept. 1969; 4pp.

Corrosion of carbon steel or Al by superphosphoric acid ammoniated to pH 6 is inhibited by adding NO_3^- ions to the solution. For example, carbon steel (ASTM A-285 Grade B) specimens exposed to circulating 10-34-0 grade solution at pH 6.0 and a temperature of 36° were corroded at a rate of 21-22.4 mils/yr. Addition of 2 wt/% of a solution containing 45.1% NH_4NO_3, 34.8% urea, and 20.1% water, decreased the corrosion rate to 4.7-4.9 mils/yr. A similar test with Al alloy (AA 5454-H34) showed a corrosion rate of 66.5-67.4 mils/Yr for uninhibited 10-34.0 solution, and 28.1-28.7 mils/Yr for solution inhibited with NH_4NO_3-urea solution. Cf. U.S. 3,617, 240:FA 5,174.

[*Fertilizer Abstracts*, **5** (9) (1972), 222]

Phosphoric Acid and Phosphate Fertilizer

A. G. Betts.
U.S. 3,671,189, June 20, 1972, Appl. June 16, 1966; 9pp.

In decomposing phosphate rock with an acid to produce H_3PO_4 or fertilizers, the presence of a soluble Al salt of the acid prevents formation of fluosilicates or volatile F compounds (Cf. U.S. 3,489,510: FA 3,475), permits recovery of commercial by-product Al Fluorides, produces H_3PO_4 low in F and Al, and permits the use of SO_2 for decomposing the phosphate rock. For example, 10 parts Al $(OH)_3$ was dissolved in 84 parts H_2SO_4 and to the solution was added 100 parts of powdered phosphate rock containing P_2O_5 32.8, CaO 47.8, and F 3.9%. No F compounds were volatilized. The reaction mixture was filtered to remove gypsum, and to the filtrate was added NaF 15.7, and HF 2.5 parts, causing precipitation of 23 parts of Na_3AlF_6. In another example, a slurry was prepared from powdered phosphate rock 100, Al_2O_3 as $Al(OH)_3$ 9, and water 225 parts. The slurry was used to absorb 21 parts SO_2 from a gas stream. The reaction product can be treated with H_2SO_4 to convert the $CaSO_3$ to $CaSO_4$ and produce H_3PO_4 or a superphosphate-type product.

[*Fertilizer Abstracts*, **5** (9) (1972), 222]

Ammonium Polyphosphate Suspension Fertilizers

T. M. Jones (to Tennessee Valley Authority)
U.S. Pat. Off. Defensive Publication T900, 026, July 25, 1972, Appl. June 21, 1971; 58 pp.

Ammonium polyphosphate fertilizers are limited in grade and only short-term storage is feasible because crystals grow to large sizes during storage and high viscosities develop. Large crystals settle and plug up valves and spray nozzles. Either large crystals or high viscosity makes transfer through pipe lines and disbursement to the soil difficult. Crystal growth and increase in viscosity during storage are retarded by control of acid concentration (polyphosphate level), product concentration, and pH to produce an abundance of small seed

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—Editor

crystals that remain as the equilibrium phase despite hydrolysis of polyphosphate. With acid of 76 to 78% P_2O_5 content, ammoniation to pH 5.0 to 5.4 results in $NH_4H_2PO_4$ as the equilibrium phase. Ammoniation to pH 6.3 to 7.0 results in $(NH_4)_2HPO_4$ as the equilibrium phase. Typical products are 11-45-0 (pH 5.2) or 13-41-0 and 14-44-0 (pH 6.4). Higher acid concentrations or ammoniation in the pH range 5.6 to 6.0 result in unstable crystal phases. Satisfactory high-grade, three-component suspensions with good storage properties can also be produced by this procedure.

[*Fertilizer Abstracts*, **5** (9) (1972), 223]

Urea-Ammonium Polyphosphate

R. G. Lee and R. D. Mitchell (to Tennessee Valley Authority)

U.S. Pat. Off. Defensive Publication T900, 018, July 25, 1972, Appl. Apr. 1, 1971; 17 pp.

Concentrated urea solution (95-100%), anhydrous molten ammonium polyphosphate from a reactor, and recycled fine product are fed to a pugmill. The urea solution is sprayed onto the recycle in the pugmill upstream from the feed point of the polyphosphate melt, which allows the urea to be coated by the melt and prevents subsequent dusting off of urea. Solid urea, $(NH_4)_2SO_4$, KCl, or micronutrient sources can also be fed to the pugmill. The granules from the pugmill are cooled, screened, and the fines crushed oversize are recycled to the pugmill.

[*Fertilizer Abstracts*, **5** (9) (1972), 223]

Ammonium Polyphosphates

E. C. Camp and H. J. Clausen (to Cities Service Co.).

U.S. 3,661,551, May 9, 1972, Appl. May 4, 1970; 7 pp.

Superphosphoric acid containing 60-85% P_2O_5 is admixed with water to bring the concentration to 52-56% P_2O_5. The temperature of dilution is 77-135°F. At the lower temperature the diluted acid is ammoniated within about 1 hr; at the higher temperature the diluted acid is ammoniated within about 3 minutes, to avoid significant hydrolysis of the non-ortho acids. Ammoniation is carried out with anhydrous NH_3 while maintaining the reaction temperature below about 185°F. The exothermic heat is sufficient to vaporize a major amount of the water and produce a substantially dry ammonium polyphosphate product containing at least 90% of the polyphosphate present in the original superphosphoric acid. The method avoids the use of high temperatures and superatmospheric pressures in producing solid ammonium polyphosphate fertilizers.

[*Fertilizer Abstracts*, **5** (9) (1972), 223]

Ammonium Phosphates

Andre Roche, Robert Amanrich, and Gilbert Cousserans (to Azote et Produits Chimiques S. A.).

U.S. 3,667,904, June 6, 1972, Appl. Fr. Jan. 26, 1967; 4 pp. Continuation-part of S. African 68 00,467; FA 2,1205.

The parent patent describes ammoniation of solutions containing H_3PO_4 and HNO_3 (obtained by treating phosphate rock with HNO_3 followed by $Ca(NO_3)_2$ removal) in the presence of a C_{1-8} aliphatic alcohol to precipitate $NH_4H_2PO_4$ (pH 3-5.5), $NH_4H_2PO_4 + (NH_4)_2HPO_4$ (pH 5.5-7.5, or $(NH_4)_2HPO_4$(pH 7-5-8.5). The present patent specifies a water concentration of 8-16%. Ammoniation of solutions containing less than 8% water result in co-precipitation of NH_4NO_3 and NH_4 phosphates. No appreciable precipitation occurs on ammoniating solutions containing over 16% water.

[*Fertilizer Abstracts*, **5** (9) (1972), 223]

Production of Urea-Ammonium Sulfate

H. C. Mann (to Tennesee Valley Authority).

U.S. Pat. Off. Defensive Publication T900, 027, July 25, 1972, Appl. June 21, 1971; 22 pp.

Granular urea-$(NH_4)_2SO_4$ is produced from crystalline $(NH_4)_2SO_4$, concentrated urea solution (97-99.5%), and recycled fine product. The proportion of $(NH_4)_2SO_4$ in the mixture is varied from 15 to 70% resulting in products containing 42-29% N and 3-17% S, respectively The urea-$(NH_4)_2SO_4$ mixture in these proportions is fluid enough at 250°-325°F. to be prilled and granulated by conventional methods. Typical grades produced are 40-0-0-4S, 34-0-0-9S, and 30-0-0-13S. The use of 99.5% urea solution and solid $(NH_4)_2SO_4$ allows elimination of a drying step. Granule strength is significantly increased by the presence of $(NH_4)_2SO_4$. Unconditioned prills of grade 30-0-0-9S were stored in bulk for 6 months without caking. Unconditioned product of grade 40-0-0-4S caked in 3 months but stored for this period satisfactorily when 2% of kaolin clay conditioner was added. The critical relative humidity of these products ranges from 55 to 60% at 86°F.

[*Fertilizer Abstracts*, **5** (9)(1972), 223]

Ammonium Polyphosphate Suspension Fertilizer

F. D. Nix (to Tennessee Valley Authority).

U.S. 3,676,101, July 11, 1972, Appl. Aug. 2, 1971; 13 pp.

Clayless base suspensions having grades as high as 14-47-0 are produced by close control of the P_2O_5 content of the superphosphoric acid and chilling the reaction mixture. Acid containing 80-81% P_2O_5 is reacted at 170-180°F with NH_3 and water in a stirred vessel. The hot reaction slurry is discharged as an air-atomized spray into a body of cool oil. The quick cooling causes formation of a suspension of fine crystals of NH_4 polyphosphate having good storage properties without adding clay as a suspending agent. See FA 5,218.

[*Fertilizer Abstracts*, **5** (9) (1972), 225]

Potassium Sulfate of Small Crystal Size

J. R. Barlow and H. P. Pursell (to International Minerals & Chem. Corp.).

U.S. 3,687,639, Aug. 29, 1972, Appl. May 25, 1970; 3 pp.

Finely divided crystalline K_2SO_4 suitable for direct use in suspension fertilizers is produced from aqueous K_2SO_4 solutions of $> 90\%$ saturation by dissolving KCl of —28 mesh particle size in the solution, thereby causing the selective precipitation of K_2SO_4 crystals of < 200 mesh particle size. The K_2SO_4 solution may be a by-product solution or spent crystallizer liquor containing a small amount of a surfactant, such as disodium dodecyloxybenzine sulfonate. The amount of KCl added is 20-100% of that mutually soluble with K_2SO_4 in the aqueous solution at the final crystallization temperature. After adding the KCl, the solution is cooled to precipitate more K_2SO_4. The initial and final crystallization temperatures are within the range 80°-25°. Crystalline K_2SO_4 is removed from the solution by conventional means, such as centrifugation or filtration. Examples are given which demonstrate that K_2SO_4 crystals of —325 mesh particle size are readily produced by this process. Other examples show that Na_2SO_4 crystals fo such small size can not be produced in a similar way.

[*Fertilizer Abstracts*, **6** (1) (1973), 3]

Manufacture of Ammonium Sulfate from Gypsum

J. F. Witte and J. J. deWit.

U.S. 3,687,620, Aug. 29, 1972, Appl. Sept. 18, 1970; 5 pp.

Ammonium sulfate is produced continuously in a recycled aqueous medium by the reaction of NH_3 and Co_2 with by-product gypsum from the manufacture of wet-process H_3PO_4. Gypsum slurry prepared from one part of finely divided gypsum and three parts of an aqueous $(NH_4)_2SO_4$ solution containing 42-46 wt% of $(NH_4)_2SO_4$ is fed continuously into the recycle stream in an amount equal to 1 wt % of the total stream flow. Ammonia and CO_2 are added to the recycle stream in quantities sufficient to give a gpsum conversion of ~95%. The products of the reaction are $CaCO_3$ and $(NH_4)_2SO_4$. Heat of reaction is removed to maintain the reaction at ~65° and ensure supersaturation with $CaCO_3$. The recycle circuit contains a vessel having a diameter ~5 times that of any other portion of the circuit, a height ~5/8 of the total circuit, and capacity ~10/11 of the total circuit. In this vessel the velocity of the recycle stream is reduced by a factor of ~19; the overall retention time is ~1hr. This allows the $CaCO_3$ crystals to grow under controlled conditions. A portion of the recycle stream is drawn off at 40-5°, fed into a crystallizer, and cooled to 20-5° to crystallize an excess of $(NH_4)_2SO_4$, which is discharged as product from the bottom of the crystallizer. A slurry of $CaCO_3$ crystals in $(NH_4)_2SO_4$ solution is discharged near the top of the crystallizer. The $CaCO_3$ is removed by filtration and the filtrate, a dilute aqueous solution of $(NH_4)_2SO_4$, is recycled back to the process. Part of this filtrate is used to prepare the gypsum feed slurry, part is used to wash the $(NH_4)_2SO_4$ crystals, and part is fed back into the crystallizer.

[*Fertilizer Abstracts*, **6** (1) (1973), 5]

Chloride-Free Nitric Phosphates Containing Potassium

USS Agri-Chemicals, Inc.

Brit. 1,273,008, May 3, 1972, Appl. U.S. June 26, 1968; 9 pp.

Nitric acid, K_2SO_4 and $(NH_4)_2SO_4$ are premixed and fed to a digester where reaction with phosphate rock produces a filterable slurry of $CaSO_4$, NH_4NO_3, KNO_3, and H_3PO_4. The $CaSO_4$ is removed by filtration and treated with CO_2 and NH_3 to produce $(NH_4)_2SO_4$, which is recycled to the digestion step. The filtrate from the $CaSO_4$ removal step is concentrated, ammoniated, granulated, and dried to produce a solid fertilizer. In an example, phosphate rock containing P_2O_5 33.4, Cao 46.8, F 4.06, and SO_3 1.8% was digested at 75° by a solution of 191.4 g of 55.1% HNO_3 and 44.22 g of $(NH_4)_2SO_4$. After 15 min, 87.35 g of K_2SO_4 was added and digestion continued at 75° for 2 hr. The resulting slurry was filtered, the $CaSO_4$ cake washed with H_2O, and the washings added to the filtrate. After drying, the $CaSO_4$ cake weighed 137.6 g and the combined filtrates 734.0 g. Chemical analyses show that 97.2 and 96.6% of the total P_2O_5 was citrate-soluble and H_2O-soluble, respectively. The solid product would have an $N:P_2O_5:K_2O$ ratio of ~1.33:1:1.22. In a variation of the process, HNO_3 and K_2SO_4 are mixed and cooled to crystallize a portion of the KNO_3, which is removed as a fertilizer product. The remaining liquor is mixed with the $(NH_4)_2SO_4$ and used to digest the phosphate rock. Other steps in the process remain unchanged. In this case the final product has a primary nutrient ratio of 1:1:1 and the production of a product of grade 18-18-18 is possible.

[*Fertilizer Abstracts*, **6** (1) (1973), 6]

Elimination of Magnesium Gels in Liquid and Suspension Fertilizers Derived from Wet Acid.

T. M. Jones and A. W. Frazier (to Tennessee Valley Authority).

U.S. 3,697,247, Oct. 10, 1972, Appl. Apr. 1, 1971; 5 pp.

A process is described for preventing the formation of gels in fluid ammonium polyphosphate fertilizers, both solutions and suspensions, in which at least part of the ammonium polyphosphate is derived from wet-process H_3PO_4 containing the normal impurities including Al, Fe, Mg, and F and having Mg: AL wt ratio of 1.4-5:1. The gel formation in these fluid ammonium polyphosphate fertilizers is prevented by increasing the $Al_2O_3:MgO$ wt ratio in the fluid fertilizers to 0.9-2:1 by adding $AlPO_4$, $Al_2(SO_4)_3$,$Al(NO_3)_2$,$AlCl_3$,Al pickling liquors, or mixtures thereof to either the fluid polyphosphate fertilizers or to the wet-process H_3PO_4 prior to ammoniation. Stabilized pourable, easily pumpable, gel-free solutions and/or suspensions are then produced. Twelve examples are cited. (Cf.U.S. Patent Office, Defensive Publication, T-889,024, Aug. 31, 1971, FA 4, 1872).

[*Fertilizer Abstracts*, **6** (1) (1973), 6]

Recovery of Entrainment in the Production of Ammonium Nitrate

D. J. Newman and Rolf Falch-Muus (to Chemical Construction Corp).

U.S. 3,690,820, Sept. 12, 1972, Appl. June 13, 1969; 5 pp.

In the conventional process for the production of solid NH_4NO_3 from NH_3 and aqueous HNO_3, an improvement is described in which the neutralizer condensate containing entrained NH_4NO_3 is used to scrub solid NH_4NO_3 entrainment from the dryer exhaust gases. Dilute NH_4NO_3 liquor from the scrubbing step is fed to a remelt system where oversize and undersize product is redissolved. The resulting still dilute NH_4NO_3 liquor is passed through an indirect heat exchanger and into the remelt solution concentrator where it is concentrated under vacuum and recycled to the concentrated NH_4NO_3 liquor being fed to the prilling tower. The heat exchanger serves the dual service of heating and partially concentrating the dilute NH_4NO_3 liquor as it cools and condenses the neutralizer vapors.

[*Fertilizer Abstracts*, **6** (2) (1973, 27]

Recovery of Ammonia and Carbon Dioxide from Urea Synthesis Tail Gas

M. A DeRooy, J. D. Logemann, and H. A. A. Koenders (to Stamicabon N. V.).
U.S. 3,691,729, Sept. 19, 1972, Appl. Neth. May 30, 1970: 10 pp.

A process and apparatus are described for the title operation wherein the tail gas containing H and O, after conventional scrubbing with an aqueous media to remove most of the NH_3 and CO_2, is diluted at urea synthesis pressure with 10-100% of the CO_2 required to form a non-explosive mixture. Dilution is done in a zone at least partially surrounded by and in contact with CO_2-filled buffer zone of vol at least five times that of the mixing zone. This buffer zone is capable of absorbing the rapid increases in pressure which occur as a result of explosive reactions in the remnant tail gas mixture. The equipment consists of a two-part wash column having a gas bubble washer and an intensive gas-liquid contractor of jacketed design. The jacket is filled with CO_2; and perforations in the inner wall allow direct contact between this CO_2 and the mixing zone, forming the pressure buffer. Savings in cooling H_2O and steam requirements are said to compensate for the extra cost of the CO_2 compression. The danger of damaging explosions in the wash column is reduced or eliminated entirely.

[*Fertilizer Abstracts*, **6** (2) (1973), 27]

Purification of Phosphoric Acid by Liquid-Liquid-Extraction

K. A. Williams and D. R. Stern (to Occidental Petroleum Corp.).

U.S. 3,694,153, Sept. 26, 1972, Appl. Oct. 30, 1970; 5 pp.

Liquid H_2O immiscible organic sulfonic acids, such as dinonylnaphthalene sulfonic acid diluted with mineral spirits, are used in a closed-loop liquid-liquid extraction process to selectively remove Ca^{2+},Mg^{2+}, and Fe^{3+} impurities from aqueous crude wet-process H_3PO_4 solutions containing up to 54 wt % P_2O_6. The resulting purified aqueous H_3PO_4 phase is separated from the H_2O immiscible sulfonic acid phase that contains the extracted impurities. The impure sulfonic acid is then regenerated for recycling to the extraction step by contact with an inorganic mineral acid such as H_2SO_4. When the impure crude wet-process H_3PO_4 contains < 30 wt % P_2O_6, this process may be combined with a further closed-loop liquid-liquid extraction step in which the acid is contacted with a 5-15 vol % solution of a primary amine such as n-decylamine in an organic solvent such as mineral spirits to remove additional Fe and Al impurities as well as organics, SO^{2-},F^-, and Si^{2+}. About 0.1-0.7 vol of the primary amine solvent phase is used per vol of impure H_3PO_4. Following separation of the purified aqueous H_3PO_4 phase, the amine reagent is regenerated for recycling by contact first with an acidic halide solution, such as NaCl solution, at pH 1-4, and then with a base, such as NaOH. Five examples are cited. A H_2O-white purified H_3PO_4 showing no turbidity was produced.

[*Fertilizer Abstracts*, **6** (2) (1973), 28]

Vanadium Recovery from Wet-Process Phosphoric Acid

E. L. Koerner and M. F. Lucid (to Kerr-McGee Corp.).

U.S. 3,700,415, Oct. 24, 1972, Appl. Feb. 18, 1970; 7 pp.

Pentavalent V is continuously extracted from aqueous wet-process H_3PO_4 mixtures of pH 0.0-1-5 and containing at least 0.25 mole of $F^-{}_4$mole of V. The acid mixture is treated countercurrently at 30-50° for 1-60 min with an organic solvent, such as kerosene, containing at least one complexing agent from the preferred group tri-n-octylphosphine oxide, tris (2-ethylhexyl) phosphine oxide, tributylphosphine oxide, and triphenylphosphine oxide. Extraction is accelerated by the addition of tributylphosphate, amines, or amine salts. About 0.15-10 vol of organic solvent and complexing agent are used for each vol of the acid mixture. The immiscible organic phase containing the V is separated from the acid and the V is removed by treatment at a pH of — 5.5-5.75 with an alkaline stripping solution, preferably a 10% solution of Na_2CO_3. Vanadium is then preferably precipitated as ammonium metavanadate by treatment of the heated stripping solution with $(NH_4)_2SO_4$, followed by rapid cooling to 20-25°. The ammonium metavanadate is removed by filtration and calcined to V oxide or fused to produce flake.

[*Fertilizer Abstracts*, **6** (2) (1973), 28]

Clarification of Ammonium Phosphate Solutions

A. W. Peck (to Phillips Petroleum Co.).

U.S. 3,697,233, Oct. 10, 1972, Appl$_4$ Sept. 29, 1969; 2 pp.

The title solutions produced from wet-process H_3PO_4 and containing suspended gelatinous precipitates are clarified by introducing into the solutions at ambient temperature ~ 0.125-0.25 wt % of attapulgite or bentonite clay of 0.12-1.0 micron particle size and 100-200 m^2/g surface area, allowing the clay to settle in a quiescent state, and recovering the supernatant clarified ammonium phosphate solution. The clay may be continuously introduced into the solutions as they are stored or added batchwise. Settlings are also recovered as marketable products.

[*Fertilizer Abstracts*, **6** (2) (1973), 28]

Ammonium Polyphosphates

J. F. McCullough and R. C. Sheridan (to Tennessee Valley Authority).

U.S. *Patent Office Defensive Publication* T904,031, Nov. 21, 1972, Appl. Mar. 27, 1972; 19 pp.

A method is described for producing long-chain crystalline ammonium polyphosphates with the general formula $(NH_4)mH$ (n-m) + 2 $^{P}n^{O}{}_3$ n + 1, where n is $> \sim 50$ and the ratio of m:n is 1.04 to ~ 0.85, by thermal condensation of ammonium ortho-, pyro-, tripoly-, tetrameta-, or oligophosphates by heating in a stream of NH_3 at ~ 200-400° for ~ 1.16 hr. Any of three crystalline modifications were prepared by suitable control of the operating conditions. Both ammoniated wet-process and furnace-grade H_3PO_4 were used as feed materials, and the products were high-analysis fertilizers with $N\text{-}P_2O_5\text{-}K_2O$ grades of 13-67-0 to 14-73-0.

[*Fertilizer Abstracts*, **6** (2) (1973), 29]

Monoammonium Phosphate Production

R. G. Lee and M. M. Norton (to Tennessee Valley Authority).

U.S. *Patent Office Defensive Publication* T904,033, Nov. 21, 1972, Appl. May 26 1972; 11 pp.

A process is described for the production of monoammonium phosphate in finely divided granular form containing up to 30% of its P_2O_5 as polyphosphate. Orthophosphoric acid typically containing 54% P_2O_5 is ammoniated in two stages utilizing heat from the reaction to evaporate H_2O and produce essentially anhydrous, molten monoammonium phosphate. [See U.S. 3,382,059 (FA 1,792)]. Gaseous NH_3 is fed to the first stage at a rate to give 2-6 wt % N in the acid, resulting in temperatures of 220-85° F. and evaporation of up to half of the free H_2O from the acid. The remainder of the NH_3 is added to the second stage, consisting of a pipe reactor with length-diameter ratio 11:1-74:1, to increase the NH_3:H_3PO_4 mole ratio to 0.9-1.1 and the temperature to 350-440° F., thereby evaporating all the remaining free H_2O, from the orthophosphate. The melt is cooled and solidified by mixing with recycled product, typically in a pugmill, at a ratio of recycle: melt of 3:1. The product is useful as an intermediate in the production of granular or fluid mixed fertilizers.

[*Fertilizer Abstracts*, **6** (2) (1973), 29]

Anticaking Agent for Urea

J. J. Jasnosz (to Petrochemicals, Inc.).

U.S. 3,690,931, Sept. 12, 1972, Appl. Mar. 4 9171; 3 pp.

Particulate or prilled urea is treated with 0.025-0.15 wt % of Mg dodecyl benzene sulfonate to produce an uncolored, nontoxic, free-flowing product that does not substantially cake upon standing. The finely-powdered anticaking agent may be dissolved in the molten urea prior to prilling, dissolved in the mother liquor prior to crystallization, sprayed on the surface of the solid urea with subsequent drying, or dry-coated on the surface by mixing in a rotary drum or other device. Inert particulate filler may also be mixed with the anticaking agent and the mixture applied to the surface of the solid urea. The effectiveness of the anticaking agent is shown in four examples which give results of penetrometer tests.

[*Fertilizer Abstracts*, **6** (2) (1973), 31]

Spray Device for Prilling

A. A. Vagin et al (to Dzerzhinsky Filial Nauch-Issled. Konstruk. Inst. Khim. Mashin.).

U.S. 3,700,364, Oct. 24, 1972, Appl. U.S.S.R. Dec. 23, 1968; 5 pp.

A spray device is described for introducing melts such as NH_4NO_3 or urea into the prilling tower. The device consists of an essentially bell-shaped steam-jacketed chamber having a circular horizontal perforated bottom plate and multiple unidirectional tangential branch pipes for supplying melt under pressure into the chamber so as to impart to the melt a continuous rotary motion above the perforated plate. Alternately, the chamber may be ring-shaped and made in the form of a toroid with a perforated bottom. The continuous rotary motion of the melt is said to reduce crystallization within the chamber, thereby reducing the clogging of the perforated bottom plate and the resulting operational problems.

[*Fertilizer Abstracts*, **6** (2) (1973), 31]

Oil-Prilled Fertilizers
J. E. Jordan (to Tennessee Valley Authority).
U.S. 3,703,364, Nov. 21, 1972, Appl. Apr. 8 1971; 10 pp.

Improvements in the oil prilling process for the production of solids urea and/or urea-ammonium phosphates are described which result in increased oil removal from the products and prevent the formation of urea adducts in liquid fertilizers prepared from these products. A prilling oil of low viscosity composed of naphthenic and/or isoparaffinic hydrocarbons is treated with 0.01-5 wt %, preferably 0.25-1 wt %, of fatty acid chosen from the group consisting of lauric, myristic, octanoic, palmitic, stearic, oleic, linoleic, and mixtures thereof. During the subsequent separation of oil from the product, the prills are washed with 0.1 lb of methanol, H_3PO_4, or mixtures thereof per lb of product. Examples indicate that the fatty acid additive reduces the oil content of the prills to ~30-40% of the value obtained when the fatty acid is omitted. After the washing step, ~80-90% of the oil had been removed from the prills.

[*Fertilizer Abstracts*, **6** (2) (1973), 31]

Coated Fertilizer
J. T. Dilday.
U.S. 3,697,245, Oct. 10, 1972, Appl. Aug. 12, 1970; 3 pp.

Tenacious coatings of supplemental materials are applied to granular fertilizers in motion by adding in order 0.5-5% of a mineral oil of lubricating viscosity, 0.1-0.5% of Ca lignosulfonate as an aqueous 50% solution, and 1-20% of the supplemental material as fine particles passing through a 200 mesh screen. The granules are maintained in motion during and after each addition until the supplemental material is uniformly coated on the granules. In an example, 1760 lb of urea prills were tumbled in a cement mixer while adding 20 lb of used motor oil. After tumbling for 1.5 min, 20 lb of an aqueous 50% solution of Ca lignosulfonate was added and tumbling was continued for 1 min. Then 200 lb of elemental S, 98% of which passed through a 325 mesh screen, was added with additional tumbling for 2 min. The product, containing N 40.5 and S 10%, was bagged and stacked 10 bags deep in warehouse storage; after 3 months, the product remained completely free-flowing.

[*Fertilizer Abstracts*, **6** (2) (1973), 31]

Potassium Dihydrogen Phosphate
E. K. Drechsel, J. B. Sardisco, and J. R. Stewart (to Pennzoil United, Inc.).
U.S. 3,697,246, Oct. 10, 1972, Appl. Oct. 16, 1970; 9 pp.

Phosphate rock or a solubilized form thereof, such as $Ca(H_2PO_4)_2$, is reacted continuously at 40-90° with sufficient 60-98% H_2SO_4 to provide 5-10 wt % excess SO_4^{2-} in the reacting mixture. To this mixture is also added, along with recycled mother liquor, sufficient aqueous 10-50% $KSHO_4$ to produce the KH_2PO_4 in solution. The $KHSO_4$ solution, prepared by the reaction of KCl and H_2SO_4 at ~250-300° with removal of the HCl, is added at a slow controlled rate to minimize the formation of insoluble $KHSO_4.CaSO_4$ and/or $5KHSO_4.CaSO_4$ and maintain the concentration of dissolved solids at $\leqslant 60\%$. After filtration of the reaction mixture to remove precipitated $CaSO_4$, the filtrate is treated with phosphate rock, $Ca_3(PO_4)_2$, $CaHPO_4$, $Ca(H_2PO_4)_2$, CaO, or mixtures thereof, to partially neutralize and further purify the filtrate by the precipitation of additional $CaSO_4$. After a subsequent filtration step, the resulting purified KH_2PO_4 solution is concentrated and cooled to precipitate the KH_2PO_4 which is removed by filtration, washed, and dried. The remaining filtrate (mother liquor) is recycled back to the process. Alternately, the purified KH_2PO_4 solution is mixed with an ~ equal vol of a H_2O-miscible organic solvent, such as methanol or acetone, to precipitate the KH_2PO_4. If sufficient CaO is added to raise the pH during the purification step, K_2HPO_4 may be produced by this same process.

[*Fertilizer Abstracts*, **6** (2) (1973), 32]

Phosphoric Acid Process
J. W. Markey (to Cities Service Co.).
U.S. 3,702,885, Nov. 14, 1972, Appl. July 13, 1970; 17 pp.

In the acidulation of Phosphate rock at 160-240°F. by 110-15% of the stoichiometric amount of 75-85 wt % HNO_3, the resulting acidulation mixture consists of H_3PO_4, by product $Ca(NO_3)_2$, and an excess HNO_3. The $Ca(NO_3)_2$ is precipitated at 160-90°F. in its anhydrous form by raising the concentration of HNO_3 therein until the supernatant HNO_3-H_3PO_4 solution contains < 14 wt % H_2O. The increase in HNO_3 concentration may be achieved by either adding to the acidulate 0.5-2.5 parts of 98 wt % HNO_3 per part of phosphate rock or preferably, by forming the HNO_3 *in situ* by introducing at 100-500 psig a mixture of NO_2 and/or O_2 in the proportion to give 0.75-1.20 part of N_2O_5 per part of phosphate rock. After removal of the precipitated $Ca(NO_3)_2$, there remains a mixture of H_3PO_4 and HNO_3. A method is described for reducing the HNO_3 content of the H_3PO_4 in which the acid mixture, containing < 5 wt % HNO_3, is contacted with a NO_2-free gaseous mixture of NO and O_2. Reaction with the HNO_3 produces NO_2, which is removed, and H_2O. The NO_3^-concentration of the H_3PO_4 is thereby greatly reduced. Solid $Ca(NO_3)_2$ separated from the HNO_3-H_3PO_4 mixture is washed at 70-100°F. which 80 wt % HNO_3, using at least one part of HNO_3 per part of a nitrogen oxide-or CO_2 containing atm at 1202-47°F. The nitrogen oxide decomposition gases from the fluidized bed and the NO_2 produced in the H_3PO_4 purification step are recycled to the process or they are recovered as HNO_3. Alternately, the NO used in the H_3PO_4 purification step may be obtained by the oxidation of HN_3. In an example, a mixture of H_3PO_4 52 and $HNO_3$5 wt % was contacted counter-currently with NO at 176°F. and the NO_2 was removed. The resulting product solution contained H_3PO_4 65.8 and HNO_3 ~0.4 wt %.

[*Fertilizer Abstracts*, **6** (3) (1972), 57]

Slow-Release Potassium Phosphate Fertilizers
Masao Hamamoto, Seiichi Kamo, and Kiyoshi Nakayama (to Mitsubishi Chemical Industries, Ltd.).
U.S. 3,698,885, Oct. 17, 1972, Appl. Japan Apr. 24, 1969; 11 pp.

The title fertilizers are prepared by calcining at 700-1100° for 20-30 min phosphate rock, caustic potash, and H_3PO_4 present in the P_2O_5:CaO:K_2O molar ratio of 1.O:1.7-3.7:1.2-2.0. Phosphate rock and H_3PO_4 are proportioned so that the molar ratio of P_2O_5 in the acid to that in the rock is 0.2-1.6:1.0 Addition of 0.1-5.0 wt % of B_2O_3 as borax or H_3BO_4 and 0.05-2.5 moles of MgO/mole of P_2Ot increases the citrate solubility of the product, lowers its solubility in the soil, and lowers both the calcination temperature and the reaction time. The MgO may be supplied as serpentine, forsterite, dunite, talc, enstatite, perodtite, dolomite, magnesite, brucite, magnesium sulfate, magnesium chloride, magnesium nitrate, magnesium phosphate, or mixtures thereof. After calcination, the product is sprayed at 100° with an inorganic acid or its ammonium salt to neutralize the material without increase of K water solubility. The main component of this slow-release potassium phosphate fertilizer is $CaKPO_4$, which has a H_2O-solubility of only 0.1-02 g of K_2O/100 ml of H_2O at 30°.

[*Fertilizer Abstracts*, **6** (3) (1973), 56]

Heat Recycling in Ammonia Production

Charles Dougherty (to W. R. Grace & Co.). U.S. 3,705,009, Dec. 5, 1972, Appl. June 12, 1970; 12 pp. Improvements are described in the process for the synthesis of NH_3 at 5000-15,000 psi, using reciprocating compressors, whereby essentially all of the power, heat and energy requirements of the process are supplied by heat and/or power and/or energy exchange systems within the process itself. The only outside energy supplied is the heat required in the primary reformer. Steam produced by heat recovery from the primary and secondary reformers, the shift converters, and the NH_3 converter is used to drive a steam turbine generator which produces electricity to power the electric motors driving the reciprocating compressors. Ammonia is recovered as a liquid product by indirectly cooling the effluent from the converter with H_2O to ~ 108°F. Detailed material and energy balances and details of the heat recovery and recycling steps are given (fig. 5).

[*Fertilizer Abstracts*, **6** (4) (1973), 79]

Removal of Nitrogen Oxides from Exhaust Gases. P. P.

Gertsen and T. G. Suverneva (to Permsky Politekhnichesky Institut). U.S. 3,695, 828, Oct. 3, 1972, Appl. Apr. 14, 1970; 3 pp.

Nitrogen oxides in industrial waste gases, such as tail gas from the manufacture of HNO_3, are removed or reduced to N before the exhaust gases are released to the atm. The exhaust gases are first scrubbed with milk of lime to absorb the higher oxides N_2O_3, NO_2, N_2O_4 and N_2O_5. Then the gases containing NO are passed downwardly through a layer of pyrite (FeS_2) at <0.25 mole of NO/hr/m^2 of FeS_2. During this step the FeS is sprayed with 0. 3-6 1. of H_2O/mole of NO in the gas, preferably 1.3-3 1 of H_2O mole of NO. The particulate Fe S is at least 2 mm is diameter and preferably 3-10 mm in diameter. Residual NO in the exhaust gases after contact with the FeS_2 is then reduced to N by contacting the gases for 10-15 sec with a CO-containing gas such as generator gas. All steps of the purification process are carried out at the ambient temperature of the waste gases. In an example, waste gases containing NO 3.84 and NO_2 3.16 g/m^3 were treated as described. The purified waste gases contained only 0.2 g of NO/m^3.

[*Fertilizer Abstracts*, **6** (4) (1973), 79]

Dephosphorization of Ferrophosphorus

C. M. Cosman and D. O. Buker (to American Metal Climax, Inc.). U.S. 3,699,213, Oct. 17, 1972, Appl. Dec. 24, 1969; 6 pp. Elemental P is recovered from ferrophosphorus at $\geqslant$1400°, in the presence of 5-10 wt % of Si, under a vacuum of preferably $<$ 2000 microns of Hg. The P vapor formed is removed while maintaining the vacuum and then recovered. In an example 2000 lb of ferrophosphorus containing Fe 56, P 26, V 8, Cr 6.5 Ni 2 and other elements 1.5 wt % is treated with 10 wt % of Si in the form of FeSi at 1500° and 1000 microns of Hg to produce 418 lb of elemental P and a slag composed of Fe 65, P 5 V 8.7, Ni 2.2, Si 10.9 and other elements 1.1%. This method is ideally combined with the subsequent recovery of V from the V-enriched slag and production of a final metal product containing, in the example, Fe 96, Ni 2.5, P 0.3 and other elements 1.2 wt%.

[*Fertilizer Abstracts*, **6** (4) (1973), 80]

Stabilization of Ammonium Polyphosphate Solutions

A. W. Frazier (to Tennessee Valley Authority). U.S. 3,711,268, Jan. 16, 1973 Appl. May 7, 1971; 7 pp. A process is described for the removal of Al and Mg impurities from ammonium polyphosphate fertilizer solutions derived wholly or partially from wet-process H_3PO_4. These solutions containing up to ~ 11 wt% N and 37 wt% P_2O_5, and having ~ 50% of their P_2O_5 in the form of polyphosphates, are treated with a soluble F source in amount equivalent to a sequestration ratio of 0.2-0.3 to precipitate the impurities as $MgAl(NH_4)_5(P_2O_7)_2F_2.6H_2O$. The sequestration ratio is determined by the following empirical formula: Sequestration Ratio = wt % F % wt MgO + 3 wt % Al_2O_3 + 1/3 wt % Fe_2O_3. The soluble F source is elected from the group consisting of NH_4F, NH_4HF, $(NH_4)_2SiF_6$, KF, KHF_2, K_2SiF_5, NaF, $NaHF_2$, Na_2SiF_6, HF, H_2SiF_6 and mixtures thereof. Precipitated impurities are removed by filtration. Process variables are discussed in eight examples.

[*Fertilizer Abstracts*, **6** (4) (1973), 84]

Treatment Systems for Phosphate Plant Effluent Waters

G. F. Palm. U.S. 3,699,212, Oct. 17, 1972 Appl. Sept. 19, 1968; 10 pp. Acidic waste waters containing H_3PO_4, H_2SO_4, HF, H_2SiF_6, SiF_4 and gypsum in solution are discharged during the manufacture of wet process H_3PO_4. These waste waters are treated with NH_3 and $CaSO_4$, preferably to pH 4.0-5.0, to form $(NH_4)_2SO_4$ dissolved in the waters and to precipitate the volatile F compounds as nomvolatile Ca salts. This eliminates air pollution by fluorides evolved from the ponds and stream pollution by leakage or seepage of low pH H_2O from the ponds. After separating the precipitated salts, the treated waste waters are reused in the process. The dissolved $(NH_4)_2SO_4$ in the makeup H_2O in the phosphate rock digestion step serves to reduce the overall H_2SO_4 requirement. Two treatment systems are presented, one in which water of the acid-H_2O pond and H_2O of the gypsum disposal pond are pH-adjusted separately and then mixed for reuse, with or without supplementary pH adjustment of the mixed waters, and the other in which the waters of the acid-H_2O pond having a P_2O_5 F/wt ratio of 0.02-1.5:1 and of the gypsum disposal pond having a P_2O_5:F wt ratio of 2-200: 1 are separately pH-adjusted at distinct pH levels and separately reused in the plant, with or without supplementary pH adjustment of the separate H_2O streams. Effluent scrubber waters containing acidic F and phosphate materials produced in associated diammonium phosphate and/or triple superphosphate plants may be combined with the waste waters from the H_3PO_4 plant for treatment and reuse.

[*Fertilizer Abstracts*, **6** (4) (1973), 85]

Desulfurization of Flue Gases by Fluoriferous Calcium Phosphates.

A. G. Betts. U.S. 3,697,248, Oct. 10, 1972 Appl. Dec. 31, 1970; 4 pp. Flue gases containing SO_2 are scrubbed counter-currently with an aqueous slurry composed of a finely pulverized fluoriferous Ca phosphate such as phosphate rock, apatite or Al-Ca phosphate and reactive aluminum compound selected from the group consisting of Al hydroxide, sulfate, sulfite, persulfite, phosphate, chloride and aluminate of Na, Ca, or K. The Al compound is added in sufficient amount to supply 0.5-2 wt parts of reactive Al for each part of F contained in the phosphate rock. A crude superphosphate is produced that consists of $CaSO_4$, $CaHPO_4$, an Al-F compound, and silicious components of the phosphate rock. This crude product may be further treated with H_2SO_3 under pressure, H_2SO_4, HNO_3, or Cl to solubilize the phosphate content of the crude product. The respective products are a solution of $CaH_4(PO_4)_2$, H_3PO_4, a solution of $Ca(NO_3)_2$ and a dissolved acidic compound of P, compound of P, and H_3PO_4. In an example an aqueous suspension composed of 100 parts of finely powdered precalcined phosphate rock, 1 part of Al as $Al_2(SO_4)_3$, 3 parts of Al as $NaAlO_2$, and 200 parts of H_2O was used to absorb more than 20 wt parts of SO_2.

[*Fertilizer Abstracts*, **6** (4) (1973), 85]

Purification of Wet-Process Phosphoric Acid

P.T. Chiang (to U.S. Steel Crop.). U.S. 3,707,357, Dec. 26, 1972, Appl. Mar. 23, 1971; 4 pp. Impure wet-process H_3PO_4 containing 40-70% H_3PO_4 is contacted for 10-60 min with preferably 2,2,4-trimethy-1, 3-pentanediol or 2, 2 diethyl-1,3-propanediol at a temperature at least 5° above the melting point of the solvent to extract the H_3PO_4. The solvent extract is separated from the aqueous raffinate phase and cooled to at least 20° below the melting point of the solvent for a sufficient time to crystallize $\geqslant$ 50% of the solvent, which is then separated from the mother liquor. Purified H_3PO_4 is recovered from the mother liquor, with or without H_2O stripping, by decantation. Crystallized solvent is melted and recycled to the extraction step. Thus, an impure H_3PO_4 containing P_2O_5 48.0 Fe_2O_3 0.93, Al_2O_3 1.03, MgO 0.235, F 0.66 and SO_4 2.65% was treated as described to produce a product acid containing P_2O_5 29.6, Fe_2O_3 0.27, Al_2O_3 0.15, MgO 0.032, F 0.20 and SO_4 1.17%.

[*Fertilizer Abstracts*, **6** (5) (1973), 106-07]

Calcined Phosphate Fertilizers

Rudolf Holst and Ulrich Hauschild (to Kali-Chemie A.-G.). U.S. 3,713,803, Jan. 30, 1973, Appl. Apr. 13, 1971; 5 pp. A citrate soluble calcined phosphate fertilizer is continuously produced from a mixture of phosphate rock, silica, and an alkali metal hydroxide solution which is concentrated and at least partially carbonated by CO_2 containing gases before it is incorporated in the mixture. The mixture is granulated and calcined in a rotary kiln, the hot exhaust gases are used for the preceding concentration and carbonating step. In an example, a mixture of 80 kg of sand/1000 kg of a North African phosphate rock containing P_2O_5 37.2 and CaO 50.7% was continuously fed to a paddle screw. Simultaneously the paddle screw was supplied with a hot slurry prepared by spraying 800 kg of a 50 wt % KOH solution/1000 kg of phosphate rock into the hot exhaust gases from the rotary kiln. This slurry contained total alkali equivalent to 60% KOH of which 30% was present as K_2CO_3. During mixing, calcination exhaust gases were passed through the paddle screw to increase its K_2CO_3 content, further concentrate the mixture, and produce a friable or granulated product which was immediately calcined in a rotary kiln at a maximum temperature of 1130°. The cooled and pulverized product contained P_2O_5 26.8 and K_2O 24.1%; 99.8% of the P_2O_5 was soluble in citric acid solution and 98.6% in the Petermann solution cf.*FA* 1, 1122, *FA* 2, 309; *FA* 3,322.

[*Fertilizer Abstracts*, **6** (5) (1973), 107]

Urea-Formaldehyde Fertilizers and Combination Products

R. H. Czurak and R. M. Thompson (to O. M. Scott and Sons Co.). U.S. 3,705, 794, Dec. 12, 1972, Appl. Aug. 15, 1969; 20 pp. Methods and apparatus are described for the production of particulate, foamed, slow-release urea-for-maldehyde fertilizers and their combinations with other active ingredients suitable for application to turf areas. The process consists of preparing a basic urea-formaldehyde solution of urea: formaldehyde mole ratio 1.3: 1-2.4: 1, adjusting the pH of the solution to form a noncollapsible foam, optionally prefoaming the solution with air, initiating the condensation reaction at $\geqslant$ 135°F with an acidic material, curing and heating the acidic foam at 140-220°F to complete the condensation reaction and remove H_2O, reducing the resultant material to particulate form, and optionally adding pesticides or other adjuvants. In an example, a product of 33-6-4 grade was produced from a urea-formaldehyde solution of 1.5: 1.0 urea: formaldehyde mole ratio, using KNO_3 as the source of K_2O and ammonium polyphosphate as a source of available P_2O_5 and as a catalyst to initiate the condensation reaction. The feed materials and their proportions were: Urea (45%N) 49.98, urea-formaldehyde condensate (11%N) 32.40 ammonium polyphosphate (11%N, 58% P_2O_5) 10.43, KNO_3 (13%N, 44%K_2O) 6,95 and surfactant (Calsoft F-90) 0.24 wt parts. The product contained 3.7% H_2O; 63.4% of the N was insoluble in cold H_2O; and the N availability index was 30.3%.

[*Fertilizer Abstracts*, **6** (5) (1973), 109]

Decomposable Polyolefin Agricultural Mulch

E. L. Cole, H. V. Hess, and R. C. Pomatti (to Texaco, Inc.). U.S. 3,707,056, Dec. 26, 1972, Appl. May 10, 1971; 5 PP. A degradable mixed polyolefin film which can be tilled into the soil after it has served its purpose as a mulch is described. The black film consists of low density polyethylene and up to 40% polypropylene to which 3-20% of a cation exchanged sulfonated or wet air oxidized petroleum coke is added to control the decomposition rate. Copper, Fe, Mn, Zn, Co or mixtures thereof are used to supply the cation. Fertilizers, fungicides, and nematocides may also be incorporated in the film, which contributes ion exchange capacity to the soil, furnishes nutrients and improves the tilth of the soil.

[*Fertilizer Abstracts*, **6** (5) (1973), 109]

Removal of Magnesium in the Wet-Process Phosphoric Acid Process

A W. Petersen (to Stauffer Chemical Co). U.S. 3,717,702, Feb. 20, 1973, Appl. Feb. 2, 1971; 3 pp. Prior to its digestion and reaction with H_2SO_4 to produce H_3PO_4, phosphate rock of 10-40 wt % minus-200 mesh particle size is mixed with H_2O and H_2SO_4 or SO_2 to produce a slurry containing 40-50 wt % solids. Acid is added as needed to maintain the pH of the slurry at 2.0-5.0 while mixing for 1-3 hr at 40-65°. Live steam is bubbled into the slurry to maintain this temperature. The leached rock is separated from the Mg-containing liquid phase by conventional means such as filtration, settling, or centrifugation; the liquid phase is discarded. After washing with H_2O or other suitable liquid, the leached phosphate rock of much lowered Mg content is fed into the conventional digestion system for producing H_3PO_4 using H_2SO_4. In an example, phosphate rock containing P_2O_5 31.0 and MgO 0.57 wt % was treated as described to produce a leached product containing P_2O_5 31.1 and MgO 0.31 wt %. Only 0.8% of the P_2O_5 in the rock had dissolved.

[*Fertilizer Abstracts*, **6** (6) (1973), 133]

Production of Liquid Ammonium Polyphosphate

H. C. Mann (to Tennessee Valley Authority). *U.S. Pat. Off. Defensive Publication*, T909,016, Apr. 17, 1973, Appl. Mar. 24, 1972, 24 pp. Liquid fertilizer base solutions free of noncarbonaceous precipitates and containing 80% or more of polyphosphate are produced directly from wet-process H_3PO_4, NH_3, and H_2O. The wet-process acid is partially neutralized with formation of some of the polyphosphate in a first reactor followed by further ammoniation in a second reactor, which may be of the common pipe type, where the remainder of the polyphosphate is formed. Melt from the pipe reactor is then processed directly into a liquid fertilizer. The heat of ammoniation in the first reactor is supplemented with sufficient additional heat to form sufficient polyphosphate so that on further ammoniation, melts of high polyphosphate content are formed. Resultant liquid fertilizers contain sufficient polyphosphate to sequester the Mg and other impurities that normally precipitate from liquid fertilizers made from wet-process H_3PO_4. The advantage of this process is that liquid higher in polyphosphate content than those usually made directly from wet-process superphosphoric acid and as high in polyphosphate content as those made by the TVA direct process from the wet-process superphosphoric acid can now be made with wet-process H_3PO_4 without a separate concentration step.

[*Fertilizer Abstracts*, **6** (6) (1973), 136]

High-Analysis Liquid Fertilizer

W. T. Curless (to Willchemco, Inc.). U.S. 3,711,269, Jan. 16, 1973, Appl. Sept. 17, 1970; 4 pp. A clear liquid K ammonium phosphate fertilizer of high K content is produced by the ammoniation of a K acid phosphate solution to produce concurrently a precipitated ammonium phosphate which is removed. Thus, 46.8 parts of KH_2PO_4, H_3PO_4 and 9.4 parts of H_2O was reacted with 10.2 parts of anhydrous gaseous NH_3 and the resulting slurry equilibrated for 1 hr at 35°. Filtration yielded 36.4 parts of solid ammonium phosphate and 29.5 parts of liquid fertilizer containing ~ 2, P_2O_5 30, and K_2O 31.5 %.

[*Fertilizer Abstracts*, **6** (6) (1973), 136]

Iron Analysis Reagent

C. C. Hach (to Hach Chem. Co.). U.S. 3,709,662, Jan. 9, 1973, Appl. July 20, 1970; 5 pp. A single reagent formulation for use in the spectrophotometric determination of Fe, which is capable of carrying out the multiple functions required in the spectrophotometric determination, comprises a solution of thioglycolic acid, a buffer to maintain the pH of solution at a predetermined value or range and a ferroin reagent present in an amount effective to form a colored complex with the Fe in a test sample. Superior solubilizing of the Fe in a test sample is achieved when NH_4OH serves as the buffer.

[*Fertilizer Abstracts*, **6** (6) (1973), 137]

Calcium Sulfate Removal in the Wet-Process Phosphoric Acid Process

W. E. Rushton, G. E. Seavoy, and W. A. Morey (to Whiting Corp.). U.S. 3,715,191, Feb. 6, 1973, Appl. July, 13, 1970; 8 pp. An apparatus and method is described for improving the filterability of reaction slurry produced in the wet process for manufacturing H_3PO_4. The reaction slurry is classified to produce at last two fractions, one of which contains substantially all of the $CaSO_4$ crystals < 200 mesh in size and the other substantially all of the $CaSO_4$ crystals > 200 mesh in size. The slurry fraction containing the larger crystals is fed to the filter first. Then the slurry fraction containing the smaller crystals is deposited directly onto the larger crystals. In this way, blending of the filter media is said to be effectively prevented, thereby prolonging the life of the filter media without reducing the efficiency or capacity of the filter.

[*Fertilizer Abstracts*, **6** (7) (1973), 158]

Process for Producing Ammonium Phosphates and Polyphosphates

P. C. Poynor and W. H. Kegler. U.S. 3,723,086, Mar. 27, 1973, Appl. May 20, 1971; 3 pp. An improvement is described in the process for producing ammonium phosphates and polyphosphates by the ammoniation of merchant grade wet-process H_3PO_4 in a pipe reactor. To reduce the formation of insoluble ammonium phosphate materials that tend to deposit on the walls of the reactor and block fluid flow, 2-10% of urea, preferably 3-5%, is added to the H_3PO_4 prior to its ammoniation in the pipe reactor. In an example, a 5% solution of urea in merchant grade wet-process H_3PO_4 containing ~ 56% P_2O_5 was prepared at ambient temperature and stirred ~ hr. The urea-containing acid was heated to 200° F and fed at ~ 100 lb/hr to a pipe reactor ½-in. in diameter and 32-in. long where it was ammoniated with ~ 13.4 lb/hr of gaseous NH_3 preheated to 200°F. The resultant ammonium phosphate contained ~ 11.5% N and 57.6% P_2O_5. After operating the pipe reactor for 24 hr, only traces of insoluble ammonium phosphate compounds had formed on the walls of the reactor. Operation of the pipe reactor without addition of urea to the H_3PO_4 resulted in complete plugging of the reactor after only 9 hr of operation.

[*Fertilizer Abstracts*, **6** (7) (1973), 159]

Process for the Production of Ammonium Polyphosphate

R. S. Meline and R. G. Lee (to Tennessee Valley Authority). U.S. 3,733,191, May 15, 1973, Appl. Feb 13, 1970; 18 pp. High-analysis solid and fluid ammonium polyphosphate fertilizers of high P_2O_5 availability and high polyphosphate content are produced directly from commercial wet-process H_3PO_4 containing ~ 30-58% P_2O_5 and 1-10 wt % of metallic and other impurities by reaction with NH_3. The process employs simultaneous ammoniation, dehydration, and polyphosphate formation in an in-line reactor. The polyphosphate foam produced is passed into a disengaging vessel designed to allow escape of free H_2O from the foam prior to cooling, thereby preventing hydrolysis and maintaining the polyphosphate content at a high level. Melt discharged from the disengaging vessel has a specific gravity of ~ 1.6-1.7. Steam and NH_3 vapors expelled from the disengaging vessel are scrubbed with the feed H_3PO_4 prior to its entry into the in-line reactor. A small relatively negative pressure of ~ 1.10 in. of H_2O is maintained in the disengaging vessel and in the scrubber. The ammonium polyphosphate melt of substantially 100% availability is suitable for the production of solid, clear liquid, or suspension fertilizers by conventional methods. In an example wet-process H_3PO_4 made from uncalcined phosphate rock and containing 52.3 wt % P_2O_5 was preheated to 300°F. and fed to the scrubber at 567 lb/hr. Gaseous anhydrous NH_3 preheated to 310°F and the partially neutralized melt were then reacted in the in-line reactor to produce a foamy melt at 445°F. After treatment in the disengaging vessel for ~ 2 min, using a foam breaker speed of 1150 rpm, the ammonium polyphosphate melt product discharged at 500 lb/hr. It contained N 12.7 and P_2O_5 59.4%. All of the P_2O_5 was citrate soluble and 46% of the P_2O_5 was in a polyphosphate form.

[*Fertilizer Abstracts*, **6** (7) (1973), 160]

Purification of Urea Synthesis Effluent

Eiji Otsuka *et al* (to Mitsui Toatsu

Chemicals, Inc.). U.S. 3,725,210, Apr. 3, 1973, Appl. Japan Aug. 30, 1969; 4 pp. Unreacted CO_2 and NH_3 remaining in urea synthesis effluent after removal of the major portion of these materials by high pressure distillation are completely removed by a low pressure method. The effluent is passed through a column having a rectification zone maintained at 0.5 kg/cm^2 gauge and 60-120° head temperature, a heating zone maintained at 100-140° and a stripping zone wherein CO_2 is introduced at 0.01-0.2 mole/mole of urea in the effluent. In an example, urea synthesis effluent containing urea 204.5, NH_3 26.3, CO_2 8.6 and H_2O 107.8 parts was fed to the column operating at 2 kg/cm^2 and 125° in the heating zone; 9.0 parts of CO_2 was introduced into the stripping zone. Substantially all NH_3 and CO_2 in the effluent were removed and a urea solution containing urea 204.5 and H_2O 89.8 parts was discharged from the stripping zone at 100°. A gas mixture comprising NH_3 26.3, CO_2 17.6, and H_2O 18.0 parts was discharged from the top of the column.

[*Fertilizer Abstracts*, **6** (8) (1973), 185]

Urea-Coated Ganular Ammonium Sulfate for Bulk Blends

K. A. E. Blackmore (to Georgia-Pacific Crop.). U.S. 3,725,029, Apr. 3, 1973, Appl. Sept. 27, 1971; 3 pp. Solid $(NH_4)_2SO_4$ is agglomerated at 90-120° in a drum granulator using as a binder, a concentrated lignosulfonate solution at 70-95° and containing 30-70 wt % solids. Fermented spent sulfite liquor containing 40-50 wt % solids may be used as the binder. The granular $(NH_4)_2 SO_4$ product of 4-10 mesh is cooled to ambient-40°, coated with molten 90% urea solution, contacted with powdered urea, treated with an inter H_2O- insoluble powder such as talc or S, and heated to reduce the moisture content to $<$ 0.6%. In an example, the free-flowing product contained 26.9% N and did not cake on storage or segregate from dry-blended fertilizers.

[*Fertilizer Abstracts*, **6** (8) (1973), 185]

Ammonium Phosphate Fertilizers

Pieter Groenveld (to Cominco, Ltd.). U.S. 3,730,700, May 1, 1973, Appl. Canada July 7, 1969; 6 pp. The title product by the reaction under pressure of gaseous anhydrous NH_3 and wet-process H_3PO_4 in a confined elongated reaction zone under high velocity to prevent deposition of solid reaction products within the reaction zone and prevent back-mixing. Two reactor designs, of a modified pipe reactor type, are described; one design allows the H_3PO_4 to be fed transversely to the fast moving NH_3 stream and the other axially to the NH_3 stream. In operation H_3PO_4 preheated to 150° and containing 35-62% P_2O_5 is reacted for $<$ 0.1 sec with the NH_3 in the reaction zone at 30-80 psig. The NH_3 is fed at $>$ 10 psig above the reaction zone pressure. Linear velocity of the reaction mixture in the reaction zone, expressed as the velocity of the gaseous NH_3 entering the reaction zone, is maintained at 100-250 ft/sec. The reaction mixture discharges through a restricted opening at 480-870 ft/sec, whereby steam is flashed from the mixture. The dewatered mixture is granulated with fines to produce a solid granular ammonium phosphate. No drying of the granular product is necessary. In an example, products of nominal grade 11-48-0, 11-55-0, and 10-60-0 are produced containing only 0.1% citrate-insoluble P_2O_5.

[*Fertilizer Abstracts*, **6** (8) (1973), 187]

Liquid Ammonium Polyphosphate Fertilizer as a Fire Retardant

K. E. Nelson (to Early California dustries, Inc.). U.S. 3,730,890, May 1, 1973, Appl. Dec. 3, 1971; 3 pp. A fire-retardant composition especially adapted for aerial application consists of a suspension of attapulgite clay in ammonium polyphosphate solutions, such as the 10-34-0, 11-37-0, 12-40-0, and 13-42-0 grade liquid fertilizers, in which the clay serves to uniformly suspend normally insoluble, nonsuspendible components such as corrosion inhibitors, thickeners, coloring agents, or mixtures thereof. The concentrated suspension is diluted with H_2O for application. In an example, part of colloidal attapulgite clay and 20 parts of ammonium polyphosphate liquid fertilizer of grade 11-37-0 were intimately blended. Then 1 part of red iron oxide pigment was thoroughly mixed into the suspension. If desired, 5 parts of a polysaccharide gum per 100 parts of the suspension may be added to increase the viscosity of the final fire retardant composition. The corrosiveness of the concentrated suspension can be substantially reduced by further mixing therein 2 parts of $Na_2Cr_2O_7$/100 parts of the suspension. For application 100 parts of the concentrated suspension was diluted with 400 parts of H_2O and thoroughly mixed. Diluted suspension is effectively applied without undue dispersion to a forested area by dump dropping from an aircarft operating at 100 ft and 140 miles/hr with winds of 0-20 miles/hr.

[*Fertilizer Abstracts*, **6** (8) (1973), 188]

Sulfur-Coated Urea

A. R. Shirley and R. S. Meline (to Tennessee Valley Authority). *U.S. Pat. Off. Defensive Publication* T912,014, July 24, 1973, Appl. July 3, 1972; 32 pp. A process is described for applying a precisely uniform solid coating of fluid material on to solid substrate particles pre-heated in a rotary drum having a radiant heat source such that the surface irregularities of the particles are smoothed out by a combination of surface melting and tumbling action. The preheated particles are fed to a second rotary drum where multiple, thin, concentrically formed layers of the coating material are applied by cascading the substrate particles beneath a plurality of sequentially applied, closely controlled sprays of the coating material. In particular the process allows the coating of granular area with molten S applied under precise spraying temperatures and conditions in such a manner that the molten S evenly coats the particles and solidifies with the desired physical characteristics to form a slow-release N fertilizer at an economical cost without the use of subcoats, seal coats, microbicides, parting agents, or plasticizers. Further, it is shown by examples that the operational conditions and techniques presented constitute a substantial improvement in the process for the production of S-coated urea where additional coatings consisting of materials other than S are used. A unique spray header for pneumatic atomizing spray nozzles is described which includes the installation of an orifice immediately external to each nozzle. The flow rate of liquid is proportional to each nozzle based on the area of the opening in each orific. The coated product is rapidly cooled to control crystal structure of the applied coating material.

[*Fertilizer Abstracts*, **6** (9) (1973), 209]

Purification of Waste Water from Phosphate Plants

C. C. Legal (to W. R. Grace & Co.). U.S. 3,725,265, Apr. 3, 1973, Appl. Jan. 22, 1971; 11 pp. Acidic waste H_2O of pH 1-3 discharged from phosphate fertilizer plants and containing F 1500-5000, PO_4^{3-} (as P_2O_5) 2000-7000, So_4^{2-} 2000-5000, and SiO_2 600-900 ppm is purified in a multi-stage liming process. Sufficient $Ca(OH)_2$ solution is added to increase the pH of the waste H_2O to 5, thereby precipitating essentially SiO_2-free CaF_2, which is separated by filtration and recovered. The residual filtrate is then treated with additional $Ca(OH)_2$ solution to increase its pH to $\sim$6.5-8.5 whereby, there is obtained a second precipitate containing Ca phosphates of low F content as a major component. After separation and recovery of these phosphates, the resulting purified H_2O contains ~ 2-10 ppm of F^- and 30-80 ppm of PO_4^{3-} (as P_2O_5). In another embodiment of the process, a CaF_2 precipitate low in both SiO_2 and PO_4^{3+} is produced by carrying out the first precipitation at pH 3.5. The process is described in eight examples.

[*Fertilizer Abstracts*, **6** (9) (1973), 211]

Production of Liquid Fertilizers by Concurrent Ammoniation of Phosphoric and Nitric Acids

James Austin (to Occidental Research & Engineering, Ltd.). U.S. 3,709,675, Jan. 9, 1973, Appl. Apr. 2, 1969; 9 pp. A near neutral liquid N-P fertilizer having an N:P_2Ot ratio > 1:3.5 is produced in a tubular reactor by concurrently and continuously reacting H_3PO_4, containing polyphosphoric acid, and HNO_3 with a deficiency of NH_3 under turbulent conditions at 220-280°F to vaporize H_2O from the reacting mixture. After a retention time of 0-1 sec-15 min in the reactor, the resulting reaction liquid and steam are discharged downwardly through cooling tower where a countercurrent air stream quenches the reaction liquid to 80-150°F and removes the steam and H_2O vapor. Sufficient NH_3 and some H_2O, if necessary, is then added to the quenched reaction liquid to produce the final liquid fertilizer product. It is preferable to add the HNO_3 down-stream from the H_3PO_4 and NH_3 feed points and to keep retention time in the reactor short; this prevents hydrolysis of any polyphosphates in the H_3PO_4. In an example, the product was a liquid fertilizer of 20-20-0 grade at pH ~ 6.5 and contained ~ 56% ammonium polyphosphates; the reactor retention time was ~ 0.1 sec. See ger. Offen. 1,914,811 (*FA* 4, 771) and Brit. 1, 266,133 (*FA* 5, 1664).

[*Fertilizer Abstracts*, **6** (9) (1973), 213]

Suspension Fertilizers from Wet-Process Ortho-phosphoric Acids

L. A. Kendrick (to Tennessee Valley Authority). *U.S. Pat. Off. Defensive Publication* T912,015, July 24, 1973, Appl. Aug. 28, 1972; 20 pp. Gel-like precipitates identified as hydrated Fe, Al, Mg, and other metallic compounds occur in ammonium phosphate suspension fertilizers made from wet-process H_3PO_4. These small, hydrated, amorphous precipitates either destroy or decrease the fluidity of concentrated suspensions and they cannot be pumped, poured, or distributed to the soil. During storage, viscosity increases and the products frequently solidify. The dilution, during production, required for restoring fludity decreases product grade and reduces the economic advantages gained from use of wet-process H_3PO_4. A method of preventing formation of the amorphous, hydrated, gel-like materials that are derived from impurities in the acids has been found and satisfactory fluid high-grade suspensions can be economically produced. The new process involves ammoniating the acids in two or more stages. For best results, the first stage should be operated at pH 3.5-4.5 at boiling temperature using a retention-n time of 30-60 minutes. The second stage should be maintained at ~ 160 F° using a retention tome of 5-10 minutes. The suspension, of pH ~ 5.9, may have a grade of 12-40-0 or higher.

[*Fertilizer Abstracts*, **6** (9) (1973), 214]

Largest Ammonia/Urea Plant in Italy

The largest single-train ammonia/urea plant in Italy, which is one of the biggest in the world, with a rated capacity of 1,500 tpd. anhydrous ammonia and 1,100 tpd fertilizer grade urea has been completed and commissioned by Snam-Progetti in scheduled time. The whole plant is fully centrifugal compressor based and maintains self-supporting conditions both in steam and power. The main features of the ammonia plant are: a new design waste heat boiler, water tube type for 115 kg/cm²g steam raising, and the Topsoe radial flow 2-bed quench converter with built-in heat exchanger and full opening pressure vessel.

The urea plant, designed according to the Snam Progetti ammonia stripping process, features also the first use in a urea plant of a CO_2 steam-turbine driven centrifugal compressor, delivering the gas upto 160 kg/cm²g.

[*Chem Age International*, **107** (2819) (1973), 528]

P & D Division, FCI to Aid Bangladesh

A major fertilizer plant is to be set up in Bangladesh with technical collaboration from the Fertilizer Corporation of India. A team of engineers and experts from the Planning & Development Division of FCI has just returned after detailed discussion and spot study of the project with the authorities in Bangladesh. FCI will prepare the detailed techno-economic analysis for the project which will be based on natural gas available in Bangladesh. The end-products will be ammonia and urea. The surplus fertilizer in the Bangladesh unit will be exported to India.

Outlay for Science & Technology in Fifth Plan

An outlay of Rs. 1,033.3 crores on science and technology has been provided in the Fifth Five Year Plan (1974-1979). This is more than 6 times greater than what was allotted in the Fourth Plan for the development of science and technology. The breakdown of the above outlay is as follows: food and agriculture Rs. 125 crores, atomic energy Rs. 111 crores, CSIR Rs. 104 crores and space Rs. 90 crores. NCST has adopted a combination of sectoral approach and an overview of the nation's scientific and technological effort for achieving self-reliance in the core sector of the economy such as agriculture, energy, mining, metallurgy, heavy engineering and chemicals and contributing to the basic needs of people such as housing, health and education. An important feature of the plan is the provision of investments in forward-looking areas such as design of 500 mw power plant, solar energy utilization, cryogenics, human fertility regulation technology, and development of forest and marine sources. The Fifth Plan has given high priority to the setting up of a national information system for S and T.

In order to increase research and development efforts in private industries, it has been proposed to collect industrial R and D cess in selected sector to finance the S and T plan in those sectors. The resources raised by the cess will be deposited in a special fund and will be utilized for projects of national priority. The plan also proposes to restructure research in universities and the IIT towards national needs, for which Rs. 34 crores have been earmarked for scientific and engineering research in universities.

Engineers India Ltd.

At the 8th annual general meeting held on Nov. 29, 1973, Sri M. S. Pathak, Chairman and Managing Director EIL, presented a creditworthy picture of his organization Formed in 1965, the Company started to progress rapidly when it was reconstituted into a full Government-owned company in 1967. EIL performed about 45% of the total engineering of the Madras Refinery project in 1967 and almost simultaneously commenced on the design of the off site facilities of the lubricating oil plant of M/s Lube India Ltd. Later it performed 75% of the total engineering of the Haldia Refinery project and based on this experience it was able to carry out its own responsibilities in regard to the entire process design and engineering of the project for the expansion of Cochin refinery from 2.5 to 3.5 MTA. Currently EIL is undertaking by itself 100 per cent of the process design and engineering of the Bongaigaon refinery. Following the successful completion by EIL of the petroleum coke calcination plant at Barauni in 1971, the same know how is being presently employed in setting up M/s Carbon Product Co's coke calcination plant at Calcutta.

In petrochemicals, it performed 90 per cent of the engineering of Koyali Aromatic project and is now capable of preparing process design packages based on licensed information on naphtha pretreater, cat reformer and isomerization unit and also the process design of the intermediate on non-licensed facilities, i. e. xylene separation facilities. These facilities will be employed in the design of Assam Petrochemical complex. In 1971 EIL commenced work on the engineering of Koyali Petrochemical Complex, comprising of a naphtha cracker sized to produce 130,000 tpa of ethylene and facilities for pyrolysis gasoline hydrotreating, benzene extraction, butadiene extraction, polybutadiene rubber, acrcmitrite detergent alkylate, polypropylene, acrylic fibre, polyethylene and ethylene glycol. EIL has embarked on a major R and D programme in collaboration with Indian Petrochemical Corp. Ltd. at Baroda.

Regarding fertilizers EIL has empleted its engineering work for IFFCO's ammonia and SPIC's urea plant. It is fully capable of engineering, procuring and constructing non ferrous ore processing plants.

Regarding research and development, EIL is now capable of undertaking process design of the distillation train for the separation of C_8 aromatic hydrocarbons envisaged in Bongaigaon petrochemicals complex. Development work on visbreaking carried out in association with IIP has enabled it to undertake process design for the visbreaker of the Koyali refinery expansion. A 5-year programme for implementation in association with the NRDC, Indian Petrochem. Copr., IOC and IIP seeks to cover the areas of distillation and extraction technologies, extractive distillation liquid phase oxidation, liquid phase oxidation of hydrocarbons and steam cracking, visbreaking, dewaxing and deoiling, hydrogen processing of petroleum fractions and sulphur recovery, fired heaters and heat exchangers.

New Crude Gasification Process

Two Japanese companies are collaborating to commercialize a new process for gasifying crude and heavy fuel oil, using a new type of catalyst as a move towards pollution free gas generation. The process can crack and gasify naphtha, crude and even residual fuel oil by means of the catalyst and hot water. This method enables hydrogen to be directly obtained from heavy fuel oil, enabling low cost production of ammonia, methanol, etc.

[*Oil Sattistics*, **11** (2) (1973), 22]

Molten-Iron Coal Gasifier

Gasification of coal in molten-iron can produce an essentially SO_3-free off-gas suitable for shift conversion and methanation to a 920 Btu pipeline gas, according to its developer Applied Technology Corporation. Coal is crushed (—¼ inch) dried to 4 per cent moisture and fed to the gasifier. Steam is used to carry the coal into the molten iron below the surface through lances to the surface of the molten iron. Dissolved carbon in the iron is gasified by oxygen and steam to CO and hydrogen. Coal volatiles are cracked to CO, CH_4 and hydrogen, Limestone is added to yield a slag, which retains the coal sulphur. Desulphurized slag is recycled in part to utilize its lime content. Any sulphur in the desulphurization off-gas is condensed out. H_2S-SO_3 gas mixture is treated in a Claus plant for additional sulphur recovery.

Cooled off-gas is compressed and fed to a shift converter. A portion of the carbon monoxide is converted to hydrogen. This yields a gas containing hydrogen and carbon monoxide in a 3 to 1 ratio suitable for methanation. CO_3 is removed in a conventional hot carbonate scrubber. The gas is then cooled and methanated.

(*Oil Statistics*, **11**, (2) (1973), 22]

Piping Coal With Crude

The transport of low-sulphur coal from Alberta to power stations in Ontario and at intermediate location is under consideration. Using a method being developed by Shell Pac, a mixture of pulverized coal and oil could be sent through existing crude oil trunk lines. The mixture could contain upto 35% coal.

[*Oil Statistics*, **11** (2) (1973), 22]

Organic Manures and Compost

At a conference of State Agricultural Ministers and State Ministers of Urban Development and Local Self-Government, Sri Fakhruddin Ali Ahmed, Agriculture Minister, Government of India, said that as the fertilizers suppliers of W. Europe, America and Japan had expressed their inability to meet the commitments in view of the energy crises and W. Asian crisis, a nation-wide compaign should be organized to make optimum use of available fertilizer resources and to organize production of organic manures for the coming *Kharif* season. To beat the shortage of chemical fertilizers, the programme aims at making available adequate quantities of organic and green manures and farmers are to be allowed to lift urban waste manures free cost of sites where there are perpetual accumulation of huge dumps of decomposing urban wastes. He said that Gujarat had achieved good results in setting up compost plants and Delhi administration proposes to implement such schemes. He urged States to reallocate priorities in their respective plans to divert other resources for setting up these plants.

Madras Fertilizers Ltd.

With Rs. 10/- crores expansion programme, which is to begin early 1974 the NPK production at the Madras Fertilizers Ltd. near Manali is expected to go up by about 50 per cent. On completion of the expansion programme the factory will be daily producing about 1800 tes of NPK fertilizers. The entire cost of expansion, which includes a foreign exchange content of Re. 1/- crore, will be met from its own resources. The extra ammonia requirement will be made available by working the ammonia plant to its full capacity.

In its first full year of operation, MFL produced 4,12,000 tonnes of fertilizers—in terms of plant nutrients this accounted for 2,05,000 tonnes comprising 1,05,000 tes nitrogen, phosphoric acid 53,000 tes and 47,300 tes potash. During 1972-73 it wiped out its entire accumulated losses and now proposes to declare a dividend during 1973-74.

MFL has the largest single-stream ammonia plant, naphtha-based and with centrifugal compression and also the largest single stream urea and NPK granulation plants in the country. The entire production of NPK and 75% production of urea are directly bagged and distributed.

The rated capacity of the Rs. 65/- crores plant is 750 tes of ammonia, 885 tonnes of urea and 1100-1300 tonnes of NPK per day. Chemical Construction Corpr. of New York erected the factory on turn-key basis and MFL took it over on June 7, 1971. 51 per cent of its shares are held by the Government of India and the remaining is divided equally between Amoco India Inc. and the National Iranian Oil. Co.

National Income

The Central Statistical Organization Govt. of India, gave the provisional estimate of rise of national income in 1971-72 at constant (1960-61 prices) as 1.7 per cent over the previous year.

The low rate of increase (against the 4th Plan target rate of 5.5 per cent) has been the result of fall in foodgrain production in 1971-72. The manufacturing recorded a slightly higher increase of 2.8 per cent but increases in sectors other than agriculture were not large enough to compensate for the fall in agriculture. The per capita income recorded a marginal fall of 0.6 per cent during 1971-72 over 1970-71.

The per capita income of 1971-72 is estimated at Rs. 645.40 at current prices as compared to Rs. 627.50 and Rs. 345.80 in the previous year. National income in 1971-72 stood at Rs. 35,756 crores at current prices and Rs. 19,033 at 1960-61 prices.

International Agricultural Research

The member Governments and organizations of the Consultative Group on International Agricultural Research have indicated an intention to make approximately £ 33 million available in 1974 to finance international research programme aimed at raising the quantity and quality of food production in the developing countries, reports World Bank. The sum marks a continuing advance in the support given by the international community to agricultural research in developing countries. It is a third more than the members of the Group made available for 1973 and twice as much as provided in 1972, the first full year of the Group's operation.

The Consultative Group operates under the co-sponsorship of the FAO, UNDP and the World Bank Group. Among the members intending to give aid are Australia, Belgium, Canada, Denmark, the Ford Foundation, France, Germany, the International Development Research Centre, Japan, the Kellogg Foundation, Sweden, Switzerland, UK, USA, UNDP and the World Bank Group. Most of the fund will support the ongoing work of six international agricultural research centres, viz. IRRI in Philippines, International Wheat and Maize Improvement Centre in Mexico, the International Centre of Tropical Agriculture in Colombia, the International Institute of Tropical Agriculture in Nigeria, the International Potato Centre and the International Crop Research Institute of the Semi-arid Tropics in Hyderabad (India).

Indigenous Process For Potassium Carbonate

The Central Salt and Marine Chemicals Research Institute (CSIR) has developed a process for the manufacture of potassium carbonate using an ion-exchange technique.

According to the process, a solution of potassium chloride is passed through a cation-exchange resin bed, which is then washed with water. The bed is then eluted with ammonium carbonate solution and potassium carbonate is obtained in the wash liquor. By washing with potassium chloride the resin in the ammonium form is regenerated and the effluent containing ammonium chloride and potassium chloride results. Evaporation of this solution yields a mixed fertilizer containing about 28.0 per cent potash and 14.5 per cent nitrogen.

The country's annual demand for potassium carbonate is estimated to rise to 10,000 tonnes in the near future, but at present the country has only one plant, of Italian design, set up in 1968. For part of its requirements of the chemical, India depends upon imports.

[*Fert. International*, No. 43, Jan. 1973, 8]

Partial Utilization of Fertilizer Plant Capacity

The five operating units of FCI Ltd. had between them a capacity of 3.76 lakh tonnes of nitrogen during 1972-73 but the actual production was 2.76 lakh tonnes of nitrogen, amounting to about 26 per cent of the all-India production. The overall capacity utilization of the FCI units was as high as 73 per cent despite production losses due to lower level of availability of power at Nangal, power and labour problems at Gorakhpur, technological problems of the old and aging plant at Sindri,

The total fertilizer consumption during 1972-73 was 1.83 million tonnes in terms of nitrogen as against overall production of 1.06 mil tonnes by all the operating units. The gap had therefore to be filled by imports.

The following are some of the main steps being taken to improve the utilization of capacity of various units: (i) Repair and renovation of the various sections at Sindri, (ii) implementation of the Sindri Rationalization project to replace Rajasthan gypsum, (iii) implementation of the Sindri Modernization project to replace coke/coke oven gas with fuel oil, (iv) debottlenecking of the urea and NPK plants at Trombay; (v) supplementing gas availability for ammonia/methanol production at Trombay; (vi) implementing a Nangal expansion project to replace use of electricity by fuel oil for the production of ammonia; (vii) a debottlenecking project at Gorakhpur to utilize more fully the installed spare equipment; (viii) measures to overcome technological constraints in some of the sections of Udyogamandal unit of FACT; (ix) setting up facilities for supplementing the gas availability for production of ammonia at Rourkela; and (x) implementing a scheme for changing over the feedstock from lignite to fuel oil at Neyveli.

[*Oil Commentary*, **11** (6)(1973),11

Union Carbide's Coal Gasification Process

Union Carbide Corp. and Chemical Construction Corp. have signed an agreement licensing the latter to use technology developed by Union Carbide for coal gasification. Chemico will incorporate this technology with the other available processes to produce synthetic natural gas.

In Carbide's process, coal is crushed and fed to the gasifier as a dry solid or in a water slurry. It is then heated in the presence of steam by direct contact with hot ash agglomerates generated by the combustion process which produces a product containing carbon monoxide, hydrogen and about 10 per cent methane. The combustion products are essentially dust-free; they may be used to drive power recovery turbines. Simple coal preparation and coal feeding systems indicate to Carbide and Chemico engineers that the coal gasifier will be less expensive to build and operate than other methods.

[*Oil Commentary*, **11** (3) (1973), 20]

Crude From Coal and LTC Plant

The West Bengal Government has a proposal to set up a low temperature carbonization plant near Calcutta, primarily to produce coke as well as gas from coal from Raniganj coalfield using indigenous know-how. Another long-term proposal of the West Bengal Government is the idea of producing crude from coal. This conversion scheme will be evaluated by a working group of the Planning Commission.

Installed Capacity of FACT

The particulars of installed capacity and actual production of the Fertilizers and Chemicals Travancore Ltd. during 1970-71, 1971-72 and 1972-73 were as follows ('000 tonnes in terms of nutrients):

	1970-71		1971-72		1972-73	
	N	P_2O_5	N	P_2O_5	N	P_2O_5
Installed Capacity	302	35	82	53	82	35
Actual Production	33	15	40	14	31	14

[*Oil Commentary*, **11** (3) (1973), 9]

Nuclear Shale Oil Production Suggested

According to Dr. Edward Teller, Nobel Laureate nuclear physicist and 'father of the hydrogen bomb', it would be economically feasible to use underground nuclear blasts to release shale oil and thus end the U. S. dependency on imports. This plan could produce $ 3-a-barrel oil from oil shale, The nuclear blast would create a large chamber, the oil shale rubble would be burned within, air would be added to the chamber from the top and kerogen would be drawn from the chamber bottom and condensed into crude oil.

[*Oil Commentary*, **11** (3) (1973), 17]

Target of Fertilizers Production During Fifth Plan

The target of chemical fertilizers is 3.912 mil. tonnes of nitrogen and 1.174 mil. tonnes of P_2O_5 by 1978-79 according to the Approach Document for the Fifth Plan. The total installed capacity for production of fertilizers is about 1.464 mil tonnes of nitrogen and 0.5 mil te of P_2O_5 excluding the 2 new projects, viz. Goa and Cochin (Phase I), which have recently gone into production.

Several debottlenecking, renovation and modernization programmes are underway to optimize production in the existing units. In addition, several new projects/expansions are under various stages of implementation. Government have also approved in principle the setting up of 5 new projects in the public sector during the Fifth Plan period. These would be in addition to projects which are likely to be set up in the private sector.

[*Oil Commentary*, **11** (3) (1973), 6]

Gujarat State Fertilizer Co. Ltd.

With the commissioning of the sulphur dioxide and oleum plants at Baroda, GSFC has set the scene for putting on stream India's first caprolactum plant. The products of these plants will provide the feedstock for the caprolactum plant which is scheduled to go on stream shortly and for the first time replace imported caprolactum which is a prime raw material for the nylon industry.

Designed, fabricated and commissioned by Larsen and Toubro Ltd. on a turn-key basis, GSFC's sulphur dioxide and oleum plants incorporate some unique features, such as the double absorption process, by which the effluent gas is freed of polluting gases. It not only eliminates environmental hazards but also improves sulphur utilization efficiency. L and T has contributed in a big way, which includes fabrication of sophisticated equipment, like stainless steel reactor and columns, and supply of low tension switch board and valves.

STATISTICS

TABLE 1—World Nitrogen Fertilizer Production and Consumption ('000 tes)

	1969/70		1970/71		1971/72	
	Production	Consumption	Production	Consumption	Production	Consumption
Western Europe	8,162	6,304	8,207	6,860	8,554	7,343
East Europe	7,450	7,111	8,583	7,828	9,393	8,608
North America	7,582	7,037	8,057	7,631	8,250	7,690
Central America	555	762	546	799	520	858
South America	218	445	271	557	333	621
Africa	400	710	405	838	499	1,011
Asia	4,823	6,255	5,351	6,814	6,237	7,514
Oceania	183	177	155	166	170	153
WORLD TOTAL	29,373	28,801	31,575	31,493	33,956	33,798
Less losses of 1.5%*	28,932		31,101		33,447	
	+121		−392		−351	

[*Statistical Supplement* (Published by the British Sulphur Corporation Ltd., London), **No. 6** (Nov.-Dec. 1972), 16]

TABLE 2—World Phosphate Fertilizer Production and Consumption ('000 tes)

	1969/70		1970/71		1971/72	
	Production	Consumption	Production	Consumption	Production	Consumption
West Europe	5,598	5,483	5,898	5,757	6,078	6,085
East Europe	4,863	4,828	5,636	5,434	6,164	5,748
North America	5,180	4,746	5,504	4,681	5,600	4,664
Central America	152	340	185	293	233	317
South America	204	515	234	711	303	829
Africa	601	601	769	609	832	667
Asia	2,057	2,409	2,090	2,600	2,421	2,940
Oceania	1,164	1,154	1,016	1,068	1,103	1,125
WORLD TOTAL	19,975	20,076	21,332	21,153	22,734	22,375
Less losses of 1.5%*	19,675		21,012		22,393	
Difference	−401		−141		+18	

[*Statistical Supplement* (Published by the British Sulphur Corporation Ltd., London), **No. 6** (Nov.-Dec. 1972), 16]

TABLE 3—World Potash Fertilizer Production and Consumption ('000 tes)

	1969/70		1970/71		1971/72	
	Production	Consumption	Production	Consumption	Production	Consumption
West Europe	4,749	4,535	4,791	4,749	4,854	5,147
East Europe	5,590	4,793	6,506	5,250	7,233	5,808
North America	6,049	4,024	5,591	4,023	6,246	4,109
Central America	—	261	—	257	—	233
South America	17	296	21	441	23	498
Africa	67	270	166	245	274	296
Asia	428	1,449	673	1,294	463	1,376
Oceania	—	171	—	199	—	196
WORLD TOTAL	16,900	15,799	17,748	16,458	19,273	17,063
Less losses of 2.5%*	16,477	—	17,304	—	18,791	—
Less industrial grade	15,923	—	16,719	—	18,093	—
Difference	+124		+261		+430	

*This represents an estimate of losses incurred by transport, bagging and handling operations, i.e. between the production and consumption stages.

[*Statistical Supplement* (Published by the British Sulphur Corporation Ltd., London), **No. 6** (Nov.-Dec. 1972), 16]

TABLE 4—World Phosphate Rock Production and Consumption

('000 tonnes)

	1969		1970		1971	
	Production	Consumption	Production	Consumption	Production	Consumption
West Europe	100	17,451	100	17,857	90	18,783
East Europe	16,290	16,733	17,950	19,144	19,866	21,096
Africa	18,161	2,653	19,444	2,766	20,935	3,094
North America	34,223	24,224	35,143	24,946	35,277	26,432
Central America	144	610	188	848	119	973
South America	198	647	219	829	216	1,046
Asia	5,159	7,715	5,432	8,108	5,697	9,058
Oceania	2,777	3,710	2,634	3,400	2,497	3,260
WORLD TOTAL	77,052	73,747	81,110	77,898	84,694	83,742
Less lossess of 4%	73,970		77,866		81,306	
Net difference	+223		−32		−2,436	

[*Statistical Supplement* (Published by the British Sulphur Corporation Ltd., London), **No. 6** (Nov.-Dec. 1972), 9]

TABLE 5—World Sulphuric Acid Supply and Demand

(million tonnes 100% H_2SO_4)

	1969			1970			1971		
	Prod.	Cons.	Ferts.	Prod.	Cons.	Ferts.	Prod.	Cons.	Ferts.
WORLD TOTAL	88.0	89.8	n.a.	91.9	92.9	n.a.	93.9	95.3	n.a.
WESTERN WORLD TOTAL	68.4	70.6	34.2	70.1	71.6	33.1	70.6	72.5	34.2
West Europe	23.8	23.7	11.9	24.4	24.9	11.2	24.5	25.5	11.4
Africa	2.6	2.7	1.8	2.8	2.6	1.8	2.9	2.8	2.0
Asia	9.3	9.4	4.6	9.7	9.9	4.5	9.7	9.8	4.7
Oceania	2.4	2.3	1.9	2.2	2.3	1.9	2.2	2.2	2.0
North America	27.8	30.2	12.9	28.2	28.9	12.4	28.2	29.0	12.5
Central America*	1.3	1.3	0.7	1.5	1.6	0.9	1.6	1.6	1.0
South America	1.2	1.0	0.4	1.4	1.4	0.5	1.6	1.6	6.0
COMMUNIST WORLD TOTAL	19.6	19.2	n.a.	21.8	21.3	n.a	23.2	22.8	n.a.
East Europe	6.1	6.0	n.a.	6.9	6.7	n.a.	7.4	7.3	n.a.
U.S.S.R.	10.9	10.7	n.a.	12.2	12.0	n.a.	12.8	12.5	n.a.
Others†	2.6	2.5	n.a.	2.7	2.6	n.a.	3.1	3.0	n.a.

Total may not add due to rounding
n.a.—not available

*Excluding Cuba
†Total for China, North Korea, North Vietnam and Cuba

[*Statiscical Supplement* (Published by the British Sulphur Corporation Ltd., London), **No. 6** (Nov.-Dec. 1972), 6]

TABLE 6—Production of Kerosene Oil in India

Year	Public Sector	Percentage Share	Private Sector	Percentage Share	Total
1970	1861	63.9	1051	36.1	2912
1971	1909	63.7	1086	36.3	2995
1972	1861	66.2	951	33.8	2813

[*Oil Commentary*, **11** (1) (1973), 16]

TABLE 7—FERTILIZER PROJECTS OF FCI LTD.
Part 1—Units in Operation

Name of the Unit	SINDRI	NANGAL	TROMBAY	GORAKHPUR	NAMRUP
Location	Dt. Dhanbad, Bihar	Dt. Rupar, Punjab	Dt. Bombay, Maharashtra	Dt. Gorakhpur, U.P.	Dt. Lakshimpur, Assam
Date of Commissioning	30th Oct. 1951	22nd February, 1961	15th October, 1965	April, 1968	1st January, 1969
Central Investment	About Rs 40 Crores	Rs 31 Crores	Rs 49.5 Crores	Rs 35 Crores	Rs 20 Crores
Raw Materials and Utilities	*Coal*—2100 te/day. *Gypsum*—2000 te/day. *Naphtha*—50 te/day. *Pyrites* *Power*—80 MW (Capacity) *Water*—from Damodar River. 20-21 MGD	*Water* from Sutlej River. 80 MGD. *Air*—12,000 Nm^3/hr. *Power* from Bhakra Hydro-Electric Station 164 MW. *Limestone*—272 te/day. *Caustic Potash.*	Naptha *Fuel Oil*—30,000 te/yr. *Rock Phosphate*: 80,000 te/yr *Sulphur*—25,000 te/yr. *Muriate of Potash.* *Diamm. Phosphate* *Power*—Trombay Thermal Power Station 40 MW. Water—8 MGD.	*Naptha* from Barauni Refinery, IOC. 280 tonnes/day. *Coal* for raising process *Steam*—250 te/day. *Power* from U.P. State Electricity Board. 36 MW. *Water*—from Chilwa Tal Lake and Tubewells. 6 MGD.	Natural Gas from Nahorkatiya Oil Fields (M/s. Oil India Ltd.) 8 million cft. of Gas per day. *Sulphur* (Imported)—30,000 te/yr. *Power* from Namrup Thermal Power Plant of Assam State Electricity Board. 14 MW. *Water* drawn from Dilli River. 6 MGD.
Finished Products					
(i) *Fertilizers*	*Ammonium Sulphate* 960 te/day. *Amm. Sulphate Nitrate* 400 te/day. *Urea*—70 te/day.	*Calcium Ammonium Nitrate* (25% N_2)—960 te/day. content.	*Sulphala* as P_2O_5 36,000 te/yr. *Urea* (Fertilizer grade) 300 te/day.	Urea—540 te/day.	Urea—167 te/day. Amm. Sulphate—304 te/day.
(ii) *Intermediate Products and Chemicals*	*Ammonia*—459 te/day. Amm. Nitrate, Nitric acid (53%), conc, sulphuric acid, Chalk sludge, Hard Coke, Coal-Tar, Road-Tar, Motor Benzol, Pure Benzene, Refined Toluol, Xylene, Light solvent Naphtha, Naphthelene, Crude Naphthalene Pitch, Still Bottom Oil, Light Oil, Middle Oil.	*Ammonia*—307 te/day. Heavy water—14.1 te/yr. Nitric Acid (53%)—1045 te/day.	*Ammonia*——350 te/day. Methanol, Nitric acid (Tech. grade 60%). Urea (Tech. grade), sulphuric acid (98%), Amm. Bicarbonate, Argon gas, CO_2 Dry Ice, Carbon Black, Sodium Nitrate, Nitrite and Methylamines.	*Ammonia*—350 te/day.	*Ammonia*—200 te/day. Sulphuric acid—250 te/day.
Process	Synthesis Gas Production by Coal and Coke Gasification and from Naphtha by Catalytic Naphtha Steam Reformation. Amm. sulphate by S.W. Gas—Gypsum process (Merseburg Process) and also by direct acid neutralization. Urea by once through process.	Synthesis Gas Production by Electrolysis of water and Air fractionation.	Synthesis Gas Production by 'Shell' partial oxidation of Naphtha and air fractionation. Urea by Chemico's Total Recycle process.	Synthesis Gas Production 'Shell' partial oxidation of Naphtha and Air fractionation. Urea by the process of M/s. Toyo Engg. Corpn. Japan.	Catalytic Steam Reformation of Natural Gas (ICI process). Urea by Chemico's Total Recycle process.

[Compiled and Issued by Coordination Cell Chemical Research Department, P and D Div., FCI Ltd., May 21, 1973]

TABLE 8—FERTILIZER PROJECTS OF FCI LTD.,
Part 2—Units Under Execution

Name of the Unit	DURGAPUR	BARAUNI	TALCHER	RAMAGUNDAM	KORBA	HALDIA
Location	Dt. Burdwan, W.B.	Dt. Begusarai, Bihar	Dt. Dhenkanal, Orissa	Dt. Karimnagar, A.P.	Dt. Bilaspru, M.P.	Dt. Midnapore, W.B.
Raw Materials and Utilities	Naphtha from Barauni Refinery, IOC 1,76,000 te/year.	Naphtha from Barauni Refinery, IOC. 1,79,000 te/yr.	*Coal* from Talcher Coal Fields, NCDC. 1 million te/year.	*Coal* from Singareni Coal Field at Ramagundam 1 million te/year.	*Coal* from Banki and Surkachhar Colliery NCDC.	*Heavystocks* from Haldia Refinery, IOC. *Rock Phosphate*, *Sulphur* (Imported)
	Coal for raising process steam from Ranigunj Coal Fields. 1,50,000 te/year.	*Coal* for raising process steam, from Giridih, Asansol & Ranigunj Coal Fields. 1,65,000				
	Power State Electricity Board, W.B. 20 MW	*Power* Barauni Thermal Power Station of Bihar State Electricity Board. 20 MW	*Power* Orissa State Electricity Board, Talcher Thermal Station. 35 MW	*Power* from A.P. State Electricity Board. 50 MW	*Power* M.P. State Electricity Board, Korba Thermal Power Station. 59 MW	*Power* State Electricity Board, W.B.
	Water Durgapur Barrage 7-8 MGD	*Water*—Tubewells. 8.5 MGD	*Water*—Brahamani River. 15 MGD	*Water* from Godavari River. 15 MGD	*Water* from Darri Barrage of Hasdeo River. 18 MGD	*Water*—Hooghly River and Tubewells.
Finished Products	*Fertilizers* Urea—1000 te/day. (Ammonia—600 te/d).	*Fertilizers* Urea—1000 te/day. (Ammonia—600 te/d).	*Fertilizers* Urea—1500 te/day. (Ammonia—900 te/d).	*Fertilizers* Urea—1500 te/day. (Ammonia—900 te/d).	*Fertilizers* Urea—1500 te/day. (Ammonia—900 te/d).	*Fertiizers* Urea—1,65,000 te/day. Nitrophosphate—3,79,000 te/yr. (Ammonia—600 te/d). *Chemicals.* Soda Ash—200 te/de). Methanol—125 te/d).
Process	(i) Steam-Naphtha Reformation for synthesis gas. (ii) Fauser-Montecatini process for urea.	(i) Steam-Naphtha Reformation for synthesis gas. (ii) Fauser-Montecatini process based on total recycle for urea.	(i) Koppers-Totzek Coal Gasification process for synthesis gas. (ii) Gas purification by rectisol process. cess. (iii) Fauser-Montecatini process for urea.	(i) Koppers-Totzek Coal Gasification process for synthesis gas. (ii) Gas purification by Rectisol process. cess. (iii) Fauser-Montecatini process for urea	(i) Koppers-Totzek Coal Gasification process for synthesis gas. (ii) Gas purification by Rectisol process. (iii) Fauser-Montecatini process for urea.	(i) Partial Oxidation of Heavy stocks for synsis gas. (ii) Fauser-Montecatini process for urea. (iii) Ensa-Stamicarbon for Nitrophosphate.

[Complied and Issued by Coordination Cell Chemical Research Department, P and D. Div., FCI Ltd., May 21, 1973]

TABLE 9—PRODUCTION OF UREA BY COUNTRIES

(tonnes of N)

Country	Years 1966-67	1967-68	1968-69	1969-70	1970-71	1971-72
Austria	28,520	22,800	16,520	10,200	16,400	9,300
Belgium	52,538	37,999	52,563	71,392	62,766	31,528
France	83,300	66,045	78,024	82,282	117,511	55,419
Czechoslovakia	—	—	17,094	31,237	24,801	N.A.
Hungary	5,951	7,000F	30,376	42,747	70,817	81,681
Italy	187,085	265,995	300,593	281,106	310,540	343,180
Netherlands	165,475	234,166	316,137	254,168	265,242	399,708
Norway	56,800	55,200	55,500	49,400	48,600	42,700
Poland	73,146	170,751	204,039	264,230	349,846	376,878
Spain	24,200	34,500	58,520	61,000	50,000	61,000
Sweden	20,884	25,230	22,287	24,568	26,506	24,673
Mexico	—	—	70,461	73,216	79,268	130,417
USA	345,000	379,000	390,000	496,000	510,000	531,000
India	57,842	121,440	210,819	388,848	505,552	575,000
Japan	756,500	958,700	1,010,000	1,067,800	1,091,000	1,160,100
Korea, Rep.	79,379	131,646	246,235	270,423	300,164	N.A.
Kuwait	6,069	39,600	53,951	63,404	74,729	N.A.
Australia	6,000*	6,000*	N.A.	N.A.	N.A.	N.A.

Note : 1. Production of urea in the following countries is about 20,000 tonnes of N per annum: Denmark, Finland, Portugal, Switzerland, Yugoslavia, Argentina, Burma, Iseael, Philippines, Thailand.

2. About the following countries, end-product pattern of N is not fully known: Albania, Bulgaria, GDR, FDR, Rumania, U.K., USSR, Canada, Chile, Peru, Bangladesh, China, Iran, Iraq, Pakistan.

3. Production of urea in the following countries is nil: Greece, Iceland, Ireland, Brazil, Turkey, Egypt, New Zealand.

F = FAO Estimate N.A. = Not available * = Unofficial figure

Source: "Annual Fertilizer Review"—1972—FAO of UN, Rome.

[*Private Communication from C. Sahai* (FAI, New Delhi), Jan. 1974]

TABLE 10—CAPACITY OF NITROGEN (N) ACCORDING TO SOURCES OF FEEDSTOCK

(AS ON 15-10-1973)

(tonnes of nutrient N)

Stage of Production/Feedstock	Naphtha	Natural gas	Electric power	Coke/ Coke oven gas	Lignite	Imported liquid ammonia	Coal	Fuel oil	Total
I. Factories in Production	1,466,190 (75.3)	45,000 (2.3)	80,000 (4.1)	199,990* (10.3)	70,000 (3.6)	— (—)	— (—)	85,000@ (4.4)	1,946,180 (100)
II. Projects under implementation	592,000 (32.2)	367,000 (20.0)	— (—)	— (—)	— (—)	40,000 (2.2)	456,000 (24.8)	384,000@ (20.8)	1,839,000 (100)
III. Projects approved in principle	90,000 (13.2)	— (—)	— (—)	— (—)	— (—)	75,000 (11.0)	228,000 (33.4)	289,000 (42.4)	682,000 (100)
IV. Projects under consideration	— (—)	— (—)	— (—)	— (—)	— (—)	— (—)	228,000 (6.3)	3,394,000 (93.7)	3,622,00 (100)
Total	2,148,190 (26.6)	412,000 (5.1)	80,000 (1.07)	199,990 (2.5)	70,000 (0.8)	115,000 (1.4)	912,000 (11.3)	4,152,000 (51.3)	8,089,180 (100)

* Includes 27,990 tonnes of N produced as a by-product ammonium sulphate at coke-oven plants. In the case of Hindustan Steel Ltd., Rourkela, 60% of capacity of calcium ammonium nitrate is assumed from coke-oven gas and 40% from naphtha.

@ 50% of N capacity is assumed to be based on naphtha and the other 50% on fuel oil, as both these feedstocks would be supplied to the factory.

() Figures in brackets represent the percentage contribution through a fertilizer feedstock to the total (horizontal).

[*Fert. Statistics*, 1972-73 (FAI, New Delhi), Dec. 1973]

TABLE 11—CURRENT PRICES OF FERTILIZERS IN INDIA

(Rs. per tonne)

Fertilizer	Maximum Retail Price[a] (cultivator/plantation)	Effective from
(a) Statutorily Controlled		
1. Ammonium sulphate		
100 kg packing	590	October 11, 1973
50 kg packing	600	-do-
2. Urea		
46% N grade	1,050	-do-
45% N grade	1,030	-do-
3. Calcium ammonium nitrate		
26% N grade	645	-do-
25% N grade	615	-do-
(b) Imported-Pool Fertilizers		
1. Ammonium nitrophosphate 20-20-0	1,200[b]	October 11, 1973
2. Diammonium phosphate	1,335[b]	-do-
18-46-0	(1,435)*	-do-
3. NPK complex fertilizers:		
15-15-15	1,375[b]	-do-
16-16-16	1,000[b]	Nov. 20, 1972
14-14-14	859[b]	March 17, 1972
14-28-14	1,170[b]	-do-
10-26-26	1,161[b]	-do-
12-32-16	1,177[b]	-do-
14-36-13	1,271[b]	-do-
4. Mono ammonium phosphate 11-55-0	1,325	January 1, 1973
5. Muriate of potash (60% K_2O)		
100 kg packing	670	October 11, 1973
50 kg packing	680	-do-
6. Sulphate of potash (48% K_2O)	730*	March 17, 1972
	(705)*	October 11, 1973

TABLE 11 (Contd.)—CURRENT PRICES OF FERTILIZERS IN INDIA

(Rs. per tonne)

Fertilizer	Maximum Retail Price[a]	Effective from
(c) Indigenous Fertilizers (Other than Statutorily Controlled)		
1. Ammonium sulphate nitrate 26% N 50 kg packing	715[c]	October 14, 1973
2. Ammonium chloride 25% N 75 kg packing	760	October 16, 1973
3. Superphosphate 16% P_2O_5		
100 kg packing	353[d]	October 1, 1973
50 kg packing	365[d]	-do-
4. Triple superphosphate 42.5% w.s. P_2O_5		
50 kg packing	1,145.40[e]	July 23, 1973
50 kg packing (for quality less than 5 tonnes)	1,271.90[e]	-do-
5. Urea ammonium phosphate		
28-28-0 (50 kg packing)	1,493	Sept. 1, 1973
20-20-0 (50 kg packing)	1,122	-do-
14-35-14 (50 kg packing)	1,493	-do-
6. Ammonium phosphate sulphate		
16-20-0 (50 kg packing)	1,300	October 19, 1973
20-20-0 (50 kg packing)	1,400	-do-
7. Diammonium phosphate 18-46-0 (50 kg packing)	1,402	April 1, 1973
8. Nitrophosphate 15-15-15 (50 kg packing)	1,150[c]	October 14, 1973
9. NPK complex fertilizers		
17-17-17 (50 kg packing)	1,260	October 1, 1973
14-28-14 (50 kg packing)	1,430	-do-

a. These prices include the incidence of excise duty (15%), 10% was levied on March 1, 1969 and another 5% on March 17, 1972.

b. These prices include, besides the incidence of excise duty at 15% (vide a.), regulatory duty at 2 % brought into force from December 16, 1971. The latter is replaced by 5% auxiliary duty with effect from March 1, 1973.

c. Ex-factory price (inclusive of 15% excise duty).

d. Ex-factory 'port' price applicable within 161 kms of a port. It excludes the incidence of excise duty (15%).

e. F.O.R. Ambernath.

Note: 1. The maximum prices of Pool fertilizers specified above shall be exclusive of Central sales tax, local sales tax, or other local taxes wherever levied whether at the retail sale point or at any intermediate stage.

2. Pool fertilizers are delivered per tonne gross, f.o.r. works/ports freight paid by the Central Fertilizer Pool upto railhead destination by shortest and cheapest route.

( ). For use as an intermediate for manufacture of complex fertilizers and fertilizer mixtures.

* Pool issue price.

[*Fert. Statistics*, 1972-73 (FAI, New Delhi), Dec. 1973]

TABLE 12—PLANT NUTRIENTS REMOVED BY CROPS

Crop	Variety	Season	Yield in kg/ha	Nutrients removed in kg/ha N	P_2O_5	K_2O
A. Grain Crops						
(1) Paddy						
(a) Tall Indica (average)						
	Grain		2,802			
	Straw		3,604			
	Total		8,406	82	23	123
(2) Paddy[1] High Yielding Varieties						
	IR. 8	kharif	6,308	95	25	149
		rabi	6,739	99	23	124
		Total	13,047	194	48	273
	Jaya	kharif	6,138	84	25	147
		rabi	6,635	105	23	129
		Total	12,771	189	48	276
	Padma	kharif	4,954	87	22	140
		rabi	5,435	95	21	115
		Total	10,389	182	43	255
	Bala	kharif	4,262	59	19	108
		rabi	5,713	102	20	103
		Total	9,975	161	39	211
	Krishna	kharif	5,399	94	22	101
		rabi	6,574	96	23	109
		Total	11,973	190	45	210
	Cauvery	kharif	4,457	85	17	96
		rabi	5,690	88	21	116
		Total	10,147	173	38	212
	Kanchi	kharif	4,470	76	20	115
		rabi	5,785	103	24	141
		Total	10,255	179	44	256
	Ptb. 10	kharif	2,417	45	12	54
		rabi	1,800	22	8	29
		Total	4,217	67	20	83
	Mtu. 15	kharif	1,942	43	13	49
		rabi	3,242	41	13	65
		Total	5,184	84	26	114
(3) Wheat						
(a) Tall Variety (average)						
	Grain		2,242			
	Straw		4,483			
	Total		6,725	59.0	29	67
(b) Dwarf High Yeilding Varieties-						
	Grain		5,000	140-210	85-105	215-290
	Straw		7,500			
	Total		12,500			

TABLE 12 (Contd.)—PLANT NUTRIENTS REMOVED BY CROPS

Crop	Variety	Season	Yield in kg/ha	Nutrients removed in kg/ha		
				N	P_2O_5	K_2O
	(4) Jowar	Grain	1,121			
		Straw	4,483			
		Total	5,604	52	18	86
	(5) Bajra	Grain	897			
		Straw	3,587			
		Total	4,484	30	11	101
	(6) Maize	Grain	2,690			
		Straw	10,760			
		Total	13,450	114	47	105
	(7) Barley	Grain	2,466			
		Straw	4,932			
		Total	7,398	54	29	125
B.	OILSEEDS					
	(1) Groundnut seeds		1,906	78	22	45
	(2) Mustard ,,		673	22	11	28
	(3) Castor ,,		1,506	45	18	15
	(4) Linseed ,,		1,009	19	12	33
C.	SUGARCANE—(CANE)					
	in Bihar[3]		57,809	146	30	186
	in Uttar Pradesh[4]		87,109	120	89	288
	in Andhra Pradesh[5]		121,896	130	105	410
D.	FIBRE CROPS					
	(1) Cotton Lint (Rainfed)		104	26	20	84
	(2) Jute (Fibre)		1,121 to 1,681	112-280	112-123	168-224
E.	PLANTATIONS					
	(1) Rubber Latex		391	46	5.6	21.3
	(2) Coffee Cherries		628	13.8	5.0	16.9
	(3) Tee Made tea		1,009	45.4	5.0	20.2
	(4) Coconut Palms 70		40 nuts per tree	55.5	27.1	84.4
F.	OTHER CROPS					
	(1) Potato Tubers		17,575	85	30	140
	(2) Tobacco Dried leaves		1,121 to 1,345	87	19	53

Source: 1. C.R.R.I., Cuttack.

2. B. C. Wright and R. B. L. Bharadwaj, Indian Farming, 18 (12), 15-20 (Mar. 1969). Other information obtained from various Indian sources.
3. Average uptake by different varieties.
4. Average uptake under application of 135 kg N per hectare.
5. From Ankapalli Sugarcane Research Station.

[*Fert. Statistics*, 1972-73 (FAI, New Delhi), Dec. 1973]

TABLE 13—RAILWAYAFREIGHT RATES FOR FERTILIZERS IN INDIA

(Effective from 1-4-1973)

Rs./quintal

Distance in kilometers	Wagon loads			Smalls	
	Class			Class	
	42.5	45	52.2	65	75
1-40	0.73	0.76	0.85	1.21	1.36
96-100	1.17	1.23	1.40	2.02	2.29
156-160	1.49	1.59	1.79	2.60	2.96
246-250	1.87	2.07	2.38	3.48	3.98
291-300	2.19	2.31	2.66	3.89	4.45
341-350	2.41	2.54	2.94	4.31	4.93
391-400	2.64	2.78	3.21	4.70	5.40
441-450	2.86	3.02	3.49	5.12	5.88
491-500	3.08	3.25	3.76	5.53	6.35
541-550	3.29	3.47	4.02	5.92	6.78
591-600	3.50	3.69	4.27	6.29	7.22
641-650	3.71	3.91	4.53	6.67	7.67
691-700	3.91	4.13	4.79	7.06	8.11
741-750	4.12	4.35	5.05	7.44	8.54
791-800	4.33	4.57	5.30	7.82	8.99
826-850	4.52	4.78	5.54	8.17	9.40
876-900	4.71	4.98	5.78	8.52	9.80
926-950	4.90	5.18	6.01	8.88	10.20
976-1000	5.10	5.38	6.25	9.23	10.61

Note: 1. For further details see "goods Tariff—No. 32 Part II, "Goods Rate Tables" of I.R.C.A. in force from 1-4-70 and its Supplement No. 2 in force from 1-7-71.

2. Only those classes are covered which apply to fertilizer raw materials (Reference Table 10-15 of Part I).

[*Fert. Statististics* 1972-73 (FAI, New Delhi), Dec. 1973]

TABLE 14—RAILWAY FREIGHT RATES FOR FERTILIZER RAW MATERIALS IN INDIA

(Effective from 15.4.72)

Rs./quintal

Distance, kilometers	85*	105*	130*
1-40	1.25	1.50	1.81
96-100	2.14	2.59	3.16
156-160	2.14	2.59	3.16
156-160	2.78	3.38	4.14
246-250	3.74	4.57	5.61
291-300	4.18	5.11	6.28
341-350	4.63	5.67	6.97
391-400	5.07	6.22	7.65
441-450	5.52	6.77	8.34
491-500	5.96	7.32	9.01
541-550	6.38	7.83	9.65
591-600	6.80	8.35	10.29
641-650	7.21	8.86	10.93
691-700	7.63	9.38	11.56
741-750	8.05	9.89	12.20
791-800	8.46	10.41	12.84
826-850	8.84	10.88	13.42
876-900	9.23	11.35	14.01
926-950	9.61	11.82	14.59
976-1,000	9.99	12.30	15.18

	Rly Classification*		Rly Classification*
Furnace-Oil Wagonloads*	85	Naphth-Wagonloads	105
Smalls	105	Smalls	130

[*Fert. Statistics*, 1972-73 (FAI, New Delhi), Dec. 1973]

TABLE 15—PRIMARY ENERGY REQUIREMENT OF THE WORLD

(million metric tons oil equivalent)

		W. Europe	N. America	Japan	Rest of World	World
Solid Fuels	1970	306	352	62	978	1 698
	1980	240	502	105	1 299	2 146
Annual Change %0		−2.3	+3.6	+5.5	+2.9	+2.4
Liquid Fuels	1970	620	763	190	587	2 160
	1980					
Annual Change (%)		+6.0	+4.7	+9.4	+7.9	+6.5
Gaseous Fuel	1970	70	598	4	251	923
	1980	231	870	14	582	1 697
Annual Change (%)		+11.9	+3.8	+14.5	+8.8	+6.2
Primary Electricity	1970	45	50	10	30	135
	1980	173	288	50	76	587
Annual Change (%)		+13.9	+19.4	17.7	+9.9	+15.8
Total	1970	1 041	1 763	266	1 846	4 916
	1980	1 757	2 869	635	3 218	8 479
Annual Change (%)		+5.4	+5.0	+9.1	+5.7	+5.6

Source: OECD Oil Committee

[*Petroleum Press Service*, (Sept. 1973), 351]

TABLE 16—BASIC SELLING PRICES OF VARIOUS BULK REFINED PETROLEUM PRODUCTS EX-COMPANIES' STORAGE POINTS AS ON 9.11.1973

Project	Unit	Kandla	Okha	Bombay	Goa	Cochin	Madras	Vizag	Calcutta
		Rs.	Rs.	Rs.	Rs.	Rs.	Rs.	Rs.	Rs.
1. Aviation Spirit 100/130	KL	2520.34	—	2523.45	2518.17	—	2540.09	—	2549.67
2. ,, ,, 115/145	,,	—	—	2556.46	2551.28	—	2573.29	—	2582.37
3. ,, ,, 73	,,	2475.39	—	2476.68	—	2473.18	2483.53	2476.14	2498.75
4. Aviation Turbine Fuel	,,	731.29	736.32	733.71	733.55	—	753.07	746.50	751.90
5. Motor Spirit 93	,,	2525.24	—	2526.39	2521.36	2523.27	2535.18	2527.75	2549.85
6. ,, ,, 83	,,	2456.30	—	2457.00	2452.04	2454.02	2465.83	2458.40	2480.04
7. High Speed Diesel Oil	,,	699.70	699.41	697.34	695.96	696.37	708.77	702.48	709.54
8. Furnace Oil	,,	280.82	280.50	279.89	278.29	279.16	294.61	286.22	293.64
9. Kerosene Superior	,,	719.85	721.06	716.69	718.50	719.22	727.11	724.49	731.27
10. ,, Inferior	,,	364.87	366.09	361.71	363.54	364.24	372.23	369.59	376.53
11. Light Diesel Oil	,,	430.58	—	429.31	427.88	428.67	443.79	434.53	441.91
12. Bitumen Straight Grade	MT	593.13	591.71	590.23	589.93	590.01	672.92	599.59	607.06
13. ,, Cutbacks B.S. ,,	,,	706.18	704.76	703.27	702.98	703.06	715.97	712.64	720.11
14. ,, ,, R.C. ,,	,,	732.19	730.77	729.28	728.99	729.07	741.98	738.65	746.12
15. Naphtha**	,,	253.00	252.65	252.25	250.05	251.06	268.42	258.57	267.30

**Naphtha prices are exclusive of Excise Duty.

(Lok Sabha: November 13, 1973)

[*Oil Commentary*, **11** (7) (1973), 10]

TABLE 17—SALE OF KEROSENE OIL BY OIL COMPANIES IN INDIA, '000 te

	Sales by Public Sector Companies	Percentage Share	Sales by Private Sector Companies	Percentage Share	Total
1970	1977	60.6	1284	39.4	3262
1971	2321	67.1	1137	32.9	3457
1972	2413	68.9	1091	31.1	3504

[*Oil Commentary*, **11** (1) (1973) **16**]

STATEMENT ON OWNERSHIP OF TECHNOLOGY

(Based on the Declaration obtained on Sept. 5, 1964 under the Press & Registration of Books Act. 1867 as modified up to March 1, 1961)

1. Place of Publication	Planning & Development Division, Fertilizer Corporation of India Ltd., Sindri, Dhanbad, Bihar.
2. Periodicity of its publication	Quarterly
3. Printer's Name, Nationality, Address	S. N. Roye, Indian, Planning & Development Division, Fertilizer Corporation of India Ltd., Sindri Dhanbad, Bihar.
4. Publisher's Name	S. N. Roye
Nationality	Indian
Address	Planning & Development Division, Fertilizer Corporation of India Ltd., Sindri, Dhanbad, Bihar.
5. Editor's Name	S. N. Roye
Nationality	Indian
Address	Planning & Development Division, Fertilizer Corporation of India Ltd., Sindri, Dhanbad, Bihar.
6. Owner's Name	Planning & Development Division, Fertilizer Corporation of India Ltd., Sindri, Dhanbad, Bihar, which is a Government Undertaking under the administrative control of the Union Ministry of Petroleum & Chemicals.

I, Sailendra Nath Roye, declare that the particulars in respect of the said periodical are true to the best of my knowledge and belief.

S. N. ROYE
Signature of Publisher